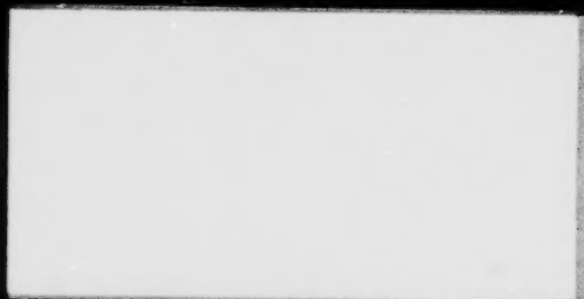


NATIONAL
URANIUM
TAILINGS
PROGRAM



ESTIMATION OF THE LIMITS OF
ACID GENERATION BY
BACTERIALLY-ASSISTED OXIDATION
IN URANIUM MILL TAILINGS
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A Research Report Prepared For:

The National Uranium Tailings Program
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MICROMEDIA
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ABSTRACT

The objective of this study was to estimate the rate and quantity of acid generated by the bacterially-assisted oxidation of sulfide minerals in uranium tailings. The rate and quantity of acid generation is a function of numerous parameters. As part of this study a computer model, the Reactive Acid Tailings Assessment Program (RATAP), was developed to analyze the effects of oxidation processes and variables on the rate and quantity of acid generation. The model was conceived as several modules which could each calibrated independently against data reported in the literature.

The integrated model was then validated against field data from two sampling stations on the Nordic tailings area in Elliot Lake, Ontario. The comparison included pH values, aqueous phase species concentrations, solid phase species concentrations and gaseous component concentrations. Overall, good agreement was found between predicted values and field observations. The results suggest that more work is required to assess the geochemistry of aluminum in order to improve model calculations.

Deterministic simulations using the validated model on a representative sulphidic tailings example indicated that the rate of pyrite oxidation exhibits a strong dependence upon temperature, bacterial population density and parameters controlling oxygen diffusion. They also indicate that bacterially-assisted oxidation predominates over chemical oxidation by approximately 6 times for acidic pH's of 3-4 and temperature of 4-15°C.

Probabilistic techniques were employed to estimate the limits of acid generation. The maximum yearly acid flux for a tailings with a water table depth of 2.0 m occurred during year two and had a mean of $250 \text{ mol.m}^{-2}.\text{yr}^{-1}$ with upper and lower limits of 30 and $870 \text{ mol.m}^{-2}.\text{yr}^{-1}$, respectively. With time, approximate time period of ten years after tailings placement, the mean flux decreased to a quasi steady state value of about $80 \text{ mol.m}^{-2}.\text{yr}^{-1}$. This suggest that as a rule of thumb, active tailings management should continue for at least a decade after tailings placement. This time scale will change

from site to site; an exact value requiring a detailed site assessment.

A sensitivity analysis of the model was also performed. The results indicated that only a few input parameters play a key role in determining the rate and quantity of acid generated. These parameters include: the biological energy of activation, bacterial population density, chemical rate constant, initial contents of aluminum hydroxide, calcite and pyrite, solubility constants for basaluminite and iron hydroxide, the air entry value, residual water content, porosity and the net rate of rainfall infiltrating.

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SENEs Consultants Limited were responsible for the development of the initial inventory, kinetics and pyrite oxidation modules. Beak Consultants Limited developed the oxygen, solute transport and speciation modules. The reaction - path-code calculations, independent calculations used to validate the model, were performed by Whiteshell nuclear Research Establishment, Atomic Energy Control Limited.

The cooperation and the assistance provided by the scientific authority, Mr. H. Steger, is gratefully acknowledged.

NOTICE

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1.0 INTRODUCTION

1.1 Scope of Work

The National Uranium Tailings Program (NUTP) was formed to conduct research into the long-term environmental behaviour of uranium mill tailings. The main objective of the NUTP is to provide a scientifically credible information base for use in developing the capability to predict the long-term effects of uranium tailings with a known degree of confidence while incorporating variability and uncertainty in the input data.

The emphasis in the research program supported by the NUTP was the development of a probabilistic assessment tool for predicting the release rate of contaminants from tailings piles and simulating their transport through the environment to humans (SENES, 1986). In other research investigations supported by the NUTP, including this study, particular attention has been given to understanding the particular geochemical processes which control the evolution of both sulphidic uranium tailings, typical of those found in the northern Ontario, and non-sulphidic uranium tailings, characteristic of those found in northern Saskatchewan. These investigations have considered physical, chemical, and biological factors at a very complex, precise scale of investigation. The stated objective of this research work was "to provide estimates of the upper and lower limits of the rate and quantity of acid generation by the bacterially-assisted oxidation of pyrite and other sulfide minerals present in uranium mill tailings."

The rate of generation of acid by bacterially-assisted oxidation of sulfide minerals in uranium and base metal mine tailings has been extensively reported in the literature (Malouf and Prater, 1961; Halbert et al., 1983; SENES, 1984). However, the interdependency of various geochemical physical and biological factors which control the rate and quantity of acid generated: such factors include parameters whose interdependency is not clearly understood; a few examples of the bacterial population density, the soil temperature, the

oxygen profile, the porewater pH, and the tailings solids buffering system.

To achieve the stated objective of this project a computer model, the Reactive Acid Tailings Assessment Program (RATAP), was developed. It is based upon principles of mass balance and employs geochemical kinetics or equilibria where appropriate and solution transport to estimate the pH and the acidity of porewater. A probabilistic technique is used to analyze the effects of oxidation processes and variables on the rate and quantity of acid generation. The model employs algorithms derived from theoretical and experimental considerations. In conjunction with the development of the model, uncertainties in the model coefficients and parameters that influence acid generation were evaluated and described by selected probability distributions.

The RATAP model comprises several modules: initial inventory; kinetics; oxygen transport; pyrite oxidation; solute transport and aqueous speciation. Detailed descriptions of the functions of the various modules are provided in the appendices. In the main report, an overview of the model, its method of coding, and results of the simulations are summarized.

In the initial inventory module, values for parameters which are assumed to be independent of any particular year, are calculated; e.g. soil temperatures. The kinetics module determines the biological and chemical rates of pyrite oxidation whereas the oxygen transport module calculates the oxygen profile. In the pyrite oxidation module the influence of oxygen on the rate of bacteria-assisted pyrite oxidation is incorporated into the computation of the amount of pyrite which is oxidized. Lastly, the solute transport and aqueous speciation modules calculates the aqueous and solid phase concentrations of various species (e.g. calcium and sulfate), the tailings porewater pH, and the acid flux leaving the tailings over time.

The individual components of each module were calibrated using actual laboratory and/or field data whenever possible. Model validation studies were then conducted using field data for the Nordic uranium tailings site in Elliot Lake, Ontario. In addition, the models calculations were also compared



against the results of a "reaction-path-code simulation" conducted by Atomic Energy of Canada Limited personnel at the Whiteshell Nuclear Research Establishment.

Following model calibration and validation, the RATAP model was run probabilistically, using data characteristic of the Elliot Lake uranium mill tailings, to assess the limits on the rate and quantity of acid generation from pyritic tailings and to identify those input parameters which most influence the model results. This information was then used to develop recommendations on those areas where emphasis should be placed in future research work.

1.2 Report Organization

This report is divided into the following sections:

- Chapter 2 Model Development presents a summary of the biological, chemical, and geochemical theory and the influence of physical factors. It summarizes the equations and associated algorithms, including the call sequence of modules over time at different layers, and the information flow between modules.
- Chapter 3 Model Validation compares the results of model calculations with field data collected at the Nordic tailings site. The comparison includes porewater pH, gaseous phase oxygen profiles, aqueous phase species concentrations and solid phase species concentrations including the residual pyrite content.
- Chapter 4 Model Calculations presents a summary of the parameters employed in the modules and their probabilistic distributions. The chapter presents the results of deterministic and probabilistic model simulations for a reference sulphidic tailings and discusses the influence of model parameters on the rate and quantity of acid generation. Finally the results of a sensitivity analysis are

used to identify the important (and conversely unimportant) parameters influencing the calculation of the rate of acid generation.

Chapter 5 Conclusions and Recommendations presents an overall summary of the model's ability to predict the bacteria-assisted oxidation of sulfide minerals in uranium tailings. Deficiencies in the model and information gaps in the input parameters are also discussed.

Appendix A-F The individual modules are described in detail in Appendices A through F. The information presented includes theoretical background, algorithms, parameter distributions, verification and sensitivity/uncertainty analyses.

Appendix G Reaction-Path-Code Calculations contains the results of chemical modelling of pyrite dissolution performed by the Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited. Reaction path simulations are presented for titrations of equilibrium and non-equilibrium assemblage of minerals using titrants of O_2 and reaction products of pyrite and pyrite plus O_2 (aqueous).

2.0 MODEL DEVELOPMENT

2.1 Introduction

The RATAP model is divided into two parts; control modules and component modules. Control modules provide the infrastructure for the probabilistic analysis of the component modules. These modules are responsible for 1) the random selection of values from specified input parameter distributions, 2) performing statistical analysis on user-specified input and calculated parameters and, 3) managing the information transfer between modules. A detailed description of the control modules is presented in SENES (1986).

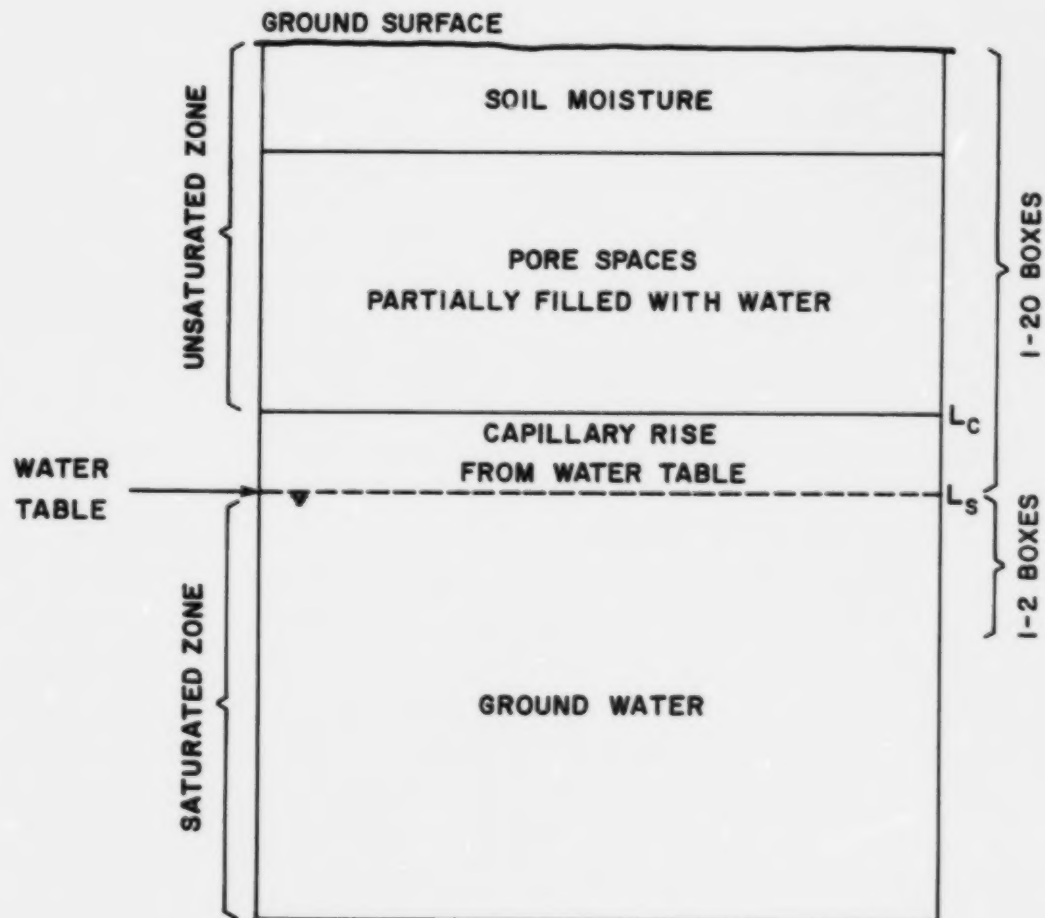
Six component modules are employed in the computer code, each performing a specific task. The modules, in order of operation, are: initial inventory, kinetics, oxygen transport, pyrite oxidation, solute transport, and aqueous speciation. The tailings soil profile employed in the control modules is subdivided into distinct layers as indicated on Figure 2.1. In the unsaturated zone and capillary fringe, one to twenty layers are employed whereas in the saturated zone, one or two layers are used. The exact number of layers are specified in the input file.

Figure 2.2 outlines the call sequence of the modules over time for the various layers. Information transferred between the modules is also identified on the figure. The first module, executed only once, is the initial inventory module which calculates for each layer the initial solids composition, the monthly soil temperature, the soil water content and soil air content. The monthly estimates are assumed to be repeated for each succeeding year.

The kinetics module, the second module, calculates rate information, (the chemical and biological oxidation rates and the oxygen consumption rate) at each time step for the various layers. The calculated parameters transferred into the model are the soil temperatures, water contents, pH and oxygen concentrations; the latter two parameters being estimates. The oxygen consumption rate information is then employed in the oxygen transport module,



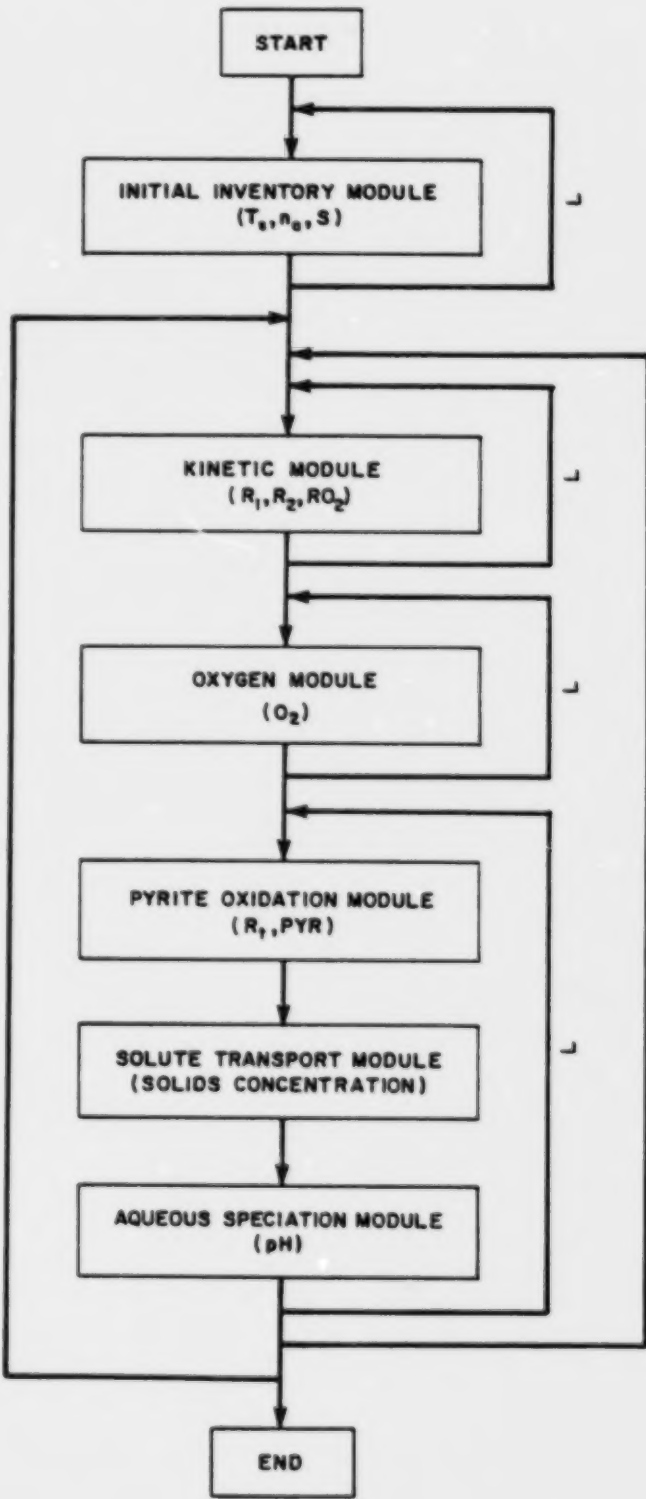
FIGURE 2.1
CONCEPT ADOPTED
FOR MODELLING OF TAILINGS



SOURCE: ADAPTED FROM EDWARD E. JOHNSON, INC. (1966)



FIGURE 2.2
CONCEPTUAL FLOW DIAGRAM



the third module, to calculate the oxygen profile. The oxygen module requires data on the volumetric air content of the soil, in addition to the rate information.

The next three modules (i.e. the pyrite oxidation, solute transport and aqueous speciation modules) are all run in sequence at time t for each layer. The pyrite oxidation module imports the biological and chemical rates of pyrite oxidation and the oxygen concentrations. The pyrite module then adjusts the rates to include the effect of oxygen concentration giving an overall rate of pyrite oxidation. The solute transport and aqueous speciation modules use the rate of pyrite oxidation to calculate the acid flux and pH, respectively. The solute transport and aqueous speciation routines are solved simultaneously.

The pH and oxygen concentrations required for the kinetics module are estimated initially using values from the previous time step. These values are then refined twice by being fed back into the kinetics module and recalculating new values. Test calculations showed that an acceptable convergence of all parameter values was achieved in three iterations. Upon completion of these calculations, the program moves onto time period $t+1$ and repeats the kinetics through aqueous speciation modules calculations.

The following section briefly outlines the individual submodules. Detailed descriptions of these submodules are presented in the appendices.

2.2 Initial Inventory Module

In the initial inventory module, initial values for those parameters that are dependent on more than one input are calculated. The parameters can be divided into two broad groups; geochemical parameters and physical parameters. These parameters are discussed briefly below; a detailed description of is presented in Appendix A.

2.2.1 Geochemical Parameters

The geochemical parameters include an initial estimate of the porewater pH, the aqueous phase concentrations and the solid phase concentrations. The pH estimate is a function of the particular scenario being analyzed, e.g. calcite present or calcite absent.

pH

The porewater pH is estimated by solving the electroneutrality equation. The concentration of other solution ions is estimated from mass balance principles if a solid phase involving the ion is not present, or from chemical equilibrium, if a controlling solid phase is present. A full development of the electroneutrality equation is given in Section 2.7.

If a particular solid phase is present which buffers pH, the solution pH can be estimated within a narrow range. Hence, the computational procedure can be greatly simplified by employing several pH equations, each applicable for only a particular pH range. Each pH equation is simplification of the electroneutrality equation; Figure 2.3 presents the various solid phase scenarios for which the pH was determined.

For conditions where calcite is present (i.e. Cases 111 to 124), an exact analytical solution is used to calculate the pH of the tailings porewater.

For conditions in which calcite is absent the computational nature of the electroneutrality equation requires that an iterative approach be used to calculate the pH. A search routine employing a step-wise increase in the estimated pH value is used to solve for the porewater pH. This approach requires that the initial estimate be less than the expected value but preferably within 0.5 units of the final calculated value for computational efficiency.

For cases where basaluminite is present (i.e. Cases 210/210 and 310/320) the initial pH estimate is based upon the time of year and hence rate of pyrite oxidation. For January, February, March and December, a starting pH of 3.5 is used whereas for the remaining months a starting pH of 3.0 is employed.

Similarly the starting pH for cases in which basaluminite is depleted (i.e. Cases 410/420 and 510/520) is 1.5 for January February, March and December and either 0.5 or 1.2 for the remaining months. A pH of 0.5 is employed when the layer above has been depleted of pyrite.

Aqueous Concentrations

For the initial conditions for the aqueous concentrations of calcium and sulfate, it is assumed that the effect of pyrite oxidation at time zero is minimal. Accordingly, the initial concentration of dissolved calcium and sulfate ions is estimated assuming equilibrium. This gives:

$$[SO_4^{2-}] = [Ca^{2+}] = (K_{CaSO_4} / f_2^2)^{0.5} \quad (2.2.1)$$

where

$[SO_4^{2-}]$ = concentration of SO_4^{2-} (mol.L⁻¹)

$[Ca^{2+}]$ = concentration of Ca^{2+} (mol.L⁻¹)

K_{CaSO_4} = solubility equilibrium constant for $CaSO_4$ (mol².L⁻⁶)

f_2 = activity coefficient for a divalent ion.

The initial solid phase concentrations are calculated using the following equation:

$$C_{si} = \rho_t X_{fi} / M_{wi} \quad (2.2.2)$$

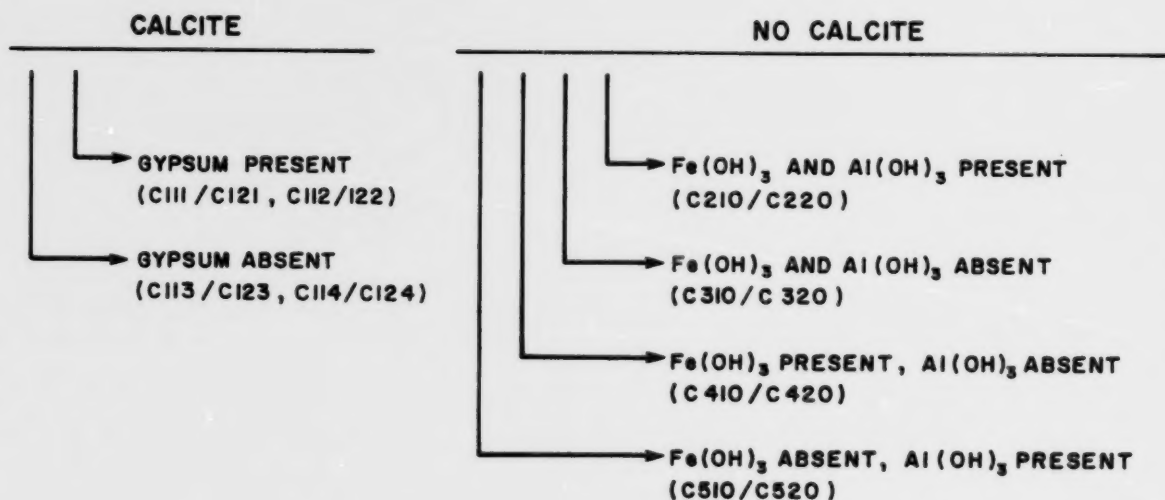
where

C_{si} = concentration of component i in solid phase (mol.m⁻³)

ρ_t = tailings bulk density (g.m⁻³)

X_{fi} = mass fraction of component i in the tailings (g/g)

FIGURE 2.3
pH COMPUTATIONAL SCENARIOS



NOTE:

C210/C220 DENOTES CASE 210 (UNSATURATED ZONE)
AND CASE 220 (SATURATED ZONE)

M_{wi} = molecular weight of component i (g.mol^{-1})

The mass fraction of the different minerals are given in Appendix A, Table A.3.2.

2.2.2 Physical Parameters

The physical parameters estimated in the initial inventory module are the soil temperature and water content. To estimate soil temperatures the following expression was fitted to Grenier and Bigu (1983) for the stanrock tailings Management site experimental data:

$$T(X,t) = T_m + A_0 [\sin(w \cdot (t - \ell) - X/d)] \exp(-X/d) \quad (2.2.3)$$

where

A_0 = empirical coefficient ($^{\circ}\text{K}$)

w = radial frequency = $2\pi/12$ mth (mth^{-1})

d = dampening depth (m)

X = actual depth of layer (m)

T_m = yearly mean temperature ($^{\circ}\text{K}$)

t = time period (mth)

ℓ = phase-shift constant; a function of the month that represents $t = 1$ (mth)

$T(X,t)$ = soil temperature at depth X at time t ($^{\circ}\text{K}$)

The water content for each layer in the unsaturated zone is determined using the following expression by:

$$n_w = (h_e/h)^\lambda (n_t - n_r) + n_r \quad (2.2.4)$$

where

h_e = the height above the water table at which air entry can occur by gravity drainage (m)

n_t = the maximum water content, i.e. porosity ($\text{m}_{\text{void}}^3 \cdot \text{m}_{\text{tail}}^{-3}$)

n_r = the residual water content ($\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{tail}}^{-3}$)

- n_w = the water content of the tailings ($m^3_{\text{water}} \cdot m^{-3}_{\text{tail}}$)
- h = height above water table (m)
- λ = soil coefficient; is the material dependent constant that is referred to as the grain size distribution parameter

The form of this equation was developed by Hillel (1980) using experimental measurements for clays and sands. The coefficient values used in this project are based upon judgement due to the lack of specific data for the Elliot Lake tailings. It is assumed that for a 10-100 year simulation period, the water content profile remains at steady state from month to month.

In the saturated zone the water content is set equal to the porosity:

$$n_w = n_t \quad (2.2.5)$$

2.3 Kinetics Module

In the kinetics module the rates of chemical and microbial oxidation of pyritic tailings are calculated. These rates are a function of several environmental parameters. Detailed descriptions of the algorithms used and their development are presented in Appendix B.

The oxidation of pyritic tailings is caused by the presence of bacteria, principally the group of *T. ferroxidans*, and a sequence of chemical reactions. Bacterially-assisted oxidation of pyrite involves both direct and indirect mechanisms. Direct mechanisms involve attack of the pyrite surface by bacteria while indirect mechanisms include the dissolution of pyrite by a ferrous ion in solution and the oxidation of ferrous iron by the bacteria. Chemical oxidation involves only the oxidation of pyrite by chemical mechanisms and the subsequent oxidation of the ferrous ion.

2.3.1 Microbial Oxidation

The rate of bacterially-assisted pyrite oxidation, R , is a function, f , of



several biological and environmental parameters (Hoffmann, et al., 1981; Halbert, et al., 1983; Jaynes et al., 1984; SENES, 1984). It may be stated by the following expression:

$$R = f(X_p, Y_{x/s}, pH, T, P_{O_2}, P_{CO_2}, S, [N], [P], E_a, A, [I]) \quad (2.3.1)$$

where

- R = rate of microbial oxidation ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)
- X_p = bacterial population density (g biomass per m^2 pyrite surface area)
- $Y_{x/s}$ = growth yield coefficient (g biomass per mol pyrite)
- pH = measure of hydronium concentration
- T = soil temperature ($^{\circ}\text{K}$)
- P_{O_2} = oxygen partial pressure (atm)
- P_{CO_2} = carbon dioxide partial pressure (atm)
- S = degree of saturation ($\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{void}}^{-3}$)
- $[N]$ = nitrate or ammonia concentration ($\text{mol} \cdot \text{m}^{-3}$)
- $[P]$ = phosphorus concentration ($\text{mol} \cdot \text{m}^{-3}$)
- $[I]$ = inhibitor concentration ($\text{mol} \cdot \text{m}^{-3}$)
- E_a = biological energy of activation ($\text{cal} \cdot \text{mol}^{-1}$)
- A = surface area of pyrite (m^2)

The overall reaction rate can be expressed as:

$$R_1 = \frac{-\mu X_p}{Y_{x/s}} \quad (2.3.2)$$

where

- R_1 = the specific reaction rate ($\text{mol} \cdot \text{m}^{-2}_{\text{tailings}} \cdot \text{mth}^{-1}$)
- μ = the specific growth rate (mth^{-1})

A multiplicative expression for the specific growth rate was selected which takes into account temperature, pH, phosphorus concentration, carbon dioxide and moisture content:

$$\mu = \mu_{\max} \left[\underbrace{\exp(C_k)}_{\text{Temperature}} \underbrace{\exp(-E_a/R_g T)}_{\text{pH}} \underbrace{(1 + 10^{2.5-\text{pH}} + 10^{\text{pH}-4.0})^{-1}}_{\text{pH}} \right. \\ \left. \underbrace{\frac{[P]}{L_p + [P]}}_{\text{Phosphorus}} \underbrace{\frac{1.3 P_{\text{CO}_2}}{10^{-4} + P_{\text{CO}_2}}}_{\text{Carbon Dioxide}} \underbrace{S}_{\text{Moisture}} \right] \quad (2.3.3)$$

where

- $\mu_{\max}$ = maximum specific growth rate observed (mth^{-1})
 L_p = limiting phosphorus concentration (mol.m^{-3})
 R_g = universal gas constant ($\text{cal.mol}^{-1}.\text{°K}^{-1}$)
 C_k = constant which sets $\mu = \mu_{\max}$ at optimal conditions

The effect of limiting oxygen concentration was not incorporated in the above equation because of the sequence of calculations, i.e. kinetics then oxygen module. The effect of oxygen concentration is included in the pyrite oxidation module.

The multiplicative form of the expression is assumed for convenience. It has not, to our knowledge, been unambiguously proven, but is widely used and is assumed to be applicable here.

The constant C_k is equal to $\mu_{\max}$ at optimal conditions. It is calculated from the following expression:

$$C_k = \ln \left[\exp(E_a/R_g T_{\text{opt}}) (1 + 10^{2.5-\text{pH}} + 10^{\text{pH}-4.0}) \right. \\ \left. \left(\frac{[P]}{L_p + [P]} \frac{1.3 P_{\text{CO}_2}}{10^{-4} + P_{\text{CO}_2}} S \right)^{-1} \right] \quad (2.3.4)$$



For the optimal conditions of:

$$\begin{aligned} \text{pH} &= 3.25 \\ T_{\text{opt}} &= 303^{\circ}\text{K} \\ E_a &= 11700 \text{ cal.mol}^{-1} \\ R_g &= 1.987 \text{ cal.mol}^{-1}.\text{K}^{-1} \\ [P] &= 2.3 \text{ mol.m}^{-3} \\ L_p &= 1.29 \times 10^{-3} \text{ mol.m}^{-3} \\ P_{\text{CO}_2} &= 3.2 \times 10^{-4} \text{ atm} \\ S &= 1.0 \text{ m}^3_{\text{water}}.\text{m}^{-3}_{\text{void}} \end{aligned}$$

C_k has a value of 19.737. The value of C_k is only changed when E_a is altered because other "optimum conditions" are invariant. E_a may change due to the imprecision in knowledge of its true (optimum) value.

2.3.2 Chemical Oxidation

The chemical rate of pyrite oxidation in an acid environment is generally much less than the biological oxidation rate at acidic pH values. It is, however, of comparable or greater than the biological rate at neutral to alkaline pH's.

As with the biological rate it is a function of several environmental parameters:

$$R = f(\text{pH}, T, E_c, A, P_{\text{O}_2}, S, [\text{Fe}^{3+}]) \quad (2.3.5)$$

where

$[\text{Fe}^{3+}]$ = concentration of the ferric ion (mol.m^{-3})

E_c = chemical energy of activation (cal.mol^{-1})

The specific rate of chemical oxidation has been expressed in the literature (McKay and Halpern, 1958) by the following expression:

$$R_2 = -r_c P_{\text{O}_2} \quad (2.3.6)$$

where

R_2 = the specific rate of chemical oxidation ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

r_c = chemical rate coefficient ($\text{mol.m}^{-2}.\text{mth}^{-1}.\text{atm}^{-1}$)

P_{O_2} = partial pressure of oxygen (atm)

The chemical rate coefficient is described by:

$$r_c = k_c \exp (-E_c/R_g T) \quad (2.3.7)$$

where

T = absolute temperature ($^{\circ}\text{K}$)

R_g = universal gas constant ($1.987 \text{ cal.mol}^{-1}.\text{}^{\circ}\text{K}^{-1}$)

k_c = chemical rate constant ($\text{mol.m}^{-2}.\text{mth}^{-1}.\text{atm}^{-1}$)

The effect of pH was not included in equation (2.3.6). Employing experimental data from Smith and Shumate (1970), the following pH expression was developed.

$$f_p = 0.25 (\text{pH})^{0.70} \quad (2.3.8)$$

where

f_p = pH factor (dimensionless)

Their data indicated that at a pH of 7.0, $f_p = 1.0$ and at pH of 2.0, $f_p = 0.4$.

The chemical rate of pyrite oxidation used in this work, then, is:

$$R_2 = f_p r_c P_{O_2} \quad (2.3.9)$$

Calibration of the expressions with the nominal values given in the appendix allows the relative significance of chemical and biological reaction to pyrite oxidation to be evaluated. At optimal biological conditions (pH=3.25, temperature =30°C, degree of saturation = 1.0, and oxygen concentration = 0.21 atm), the biological reaction rate is $6.5 \times 10^{-3} \text{ mol.m}^{-2}.\text{mth}^{-1}$ while the



chemical reaction rate is $7 \times 10^{-5} \text{ mol.m}^{-2}.\text{mth}^{-1}$. These values suggest that the biological rate is about two orders of magnitude greater than the chemical rate at optimal conditions. However, it does not support some literature which suggests that microbially mediated pyrite oxidation can exceed chemical oxidation by a factor of up to 10^6 (Singer and Stumm, 1970).

In tailings optimal biological conditions are seldom attained. Conditions suitable for maximum microbial growth will occur near the tailings surface (i.e. at a degree of saturation of 0.2 and an oxygen partial pressure of 0.21 atm) during the month of July (temperature of 25°C) after calcite has been depleted (pH of 3.6). For these conditions the biological reaction rate is $8.6 \times 10^{-4} \text{ mol.m}^{-2}.\text{mth}^{-1}$ while the chemical rate is about $5.2 \times 10^{-5} \text{ mol.m}^{-2}.\text{mth}^{-1}$. These values suggest that the biological rate is approximately 17 times greater than the chemical rate. This difference is considerably less than that described under optimal conditions.

2.4 Oxygen Module

As indicated in Section 2.3 low oxygen concentrations can limit the rate of pyrite oxidation. In the oxygen module the oxygen profile of the tailings is calculated. This information in turn is employed in the calculation of the overall rate of pyrite oxidation. In Appendix C, a detailed description of the oxygen module is presented.

There are two mechanisms by which oxygen mass transport through a porous medium occurs; advection and diffusion. In the unsaturated zone of soil the diffusive transport of oxygen through the air phase is the dominant transfer mechanism. In the capillary fringe and saturated zones of the tailings the dominant transfer mechanism is advection of oxygen dissolved in the infiltrating porewater. The physical properties of each layer in the gas-filled or non-gas filled tailings zones are used to determine whether gaseous diffusion or advection dominates. The models are described below.

2.4.1 Effective Diffusivity

Diffusive transport is a function of the effective gaseous diffusivity coefficient. The effective gaseous diffusivity (D_e) of the tailings is calculated using the following expression, experimentally determined from Nordic field data (Reardon and Moddle, 1985):

$$D_e = 52.56 \frac{n_a - 0.05}{0.95}^{1.7} \quad (2.4.1)$$

where

n_a = volumetric air content of the soil ($m_{air}^3 \cdot m_{total}^{-3}$)

D_e = effective diffusivity of oxygen ($m^2 \cdot mth^{-1}$)

This expression has a lower limit of $0.05 m_{air}^3 \cdot m_{total}^{-3}$ for n_a .

2.4.2 Diffusive Transport

The rate of response of the oxygen profile to changes in gaseous diffusion with time is relatively quick, i.e. in the order of hours compared to slower changes induced by variations in pH and temperature. Accordingly, it is appropriate to assume that the oxygen profile through the gaseous pore spaces of the tailings is at steady state in each monthly time step. This permits the development of analytical solutions for each layer. These equations are coupled to adjoining layers through the appropriate boundary conditions.

There are three possible conditions in each layer which affect the final differential equations and hence their mathematical solution. When pyrite is present, zero-order oxygen consumption kinetics are used at high oxygen concentrations ($P_{O_2} > 0.01$ atm) and first order consumption kinetics at low oxygen concentrations. This reflects the fact that oxygen consumption is independent of oxygen concentration at high oxygen concentrations. When pyrite is absent, no consumption of oxygen occurs.

For the first-order consumption reaction at steady state, the analytical solution for flux across any interval where concentrations are known at the boundaries is given as (Carslaw and Jaeger, 1959):

$$F_t = D_e (U C_1 \cosh (U dX) - U C_2) / \sinh (U dX) \quad (2.4.2)$$

and

$$F_b = D_e (U C_1 - U C_2 \cosh (U dX)) / \sinh (U dX) \quad (2.4.3)$$

where

F_t = flux at the top of the boundary layer ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)

F_b = flux at the bottom of the boundary layer ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)

C_1 = the oxygen concentration in the upper boundary layer ($\text{mol} \cdot \text{m}^{-3}$)

C_2 = the oxygen concentration in the lower boundary layer ($\text{mol} \cdot \text{m}^{-3}$)

U = square root of the ratio of the reaction rate constant (bulk) to the effective diffusivity of the layer (K_b/D_e)^{0.5} (m^{-1})

dX = thickness of a layer (m)

D_e = effective diffusivity through the tailings ($\text{m}^2 \cdot \text{mth}^{-1}$)

K_b = bulk reaction rate constant (mth^{-1})

For a zero-order consumption reaction at steady-state, the fluxes across the layer interfaces are:

$$F_t = R dX/2 + D_e C_1/dX - D_e C_2/dX \quad (2.4.4)$$

and

$$F_b = -R dX/2 + D_e C_1/dX - D_e C_2/dX \quad (2.4.5)$$

where

R = zero-order rate constant ($\text{mol.m}^{-3}.\text{mth}^{-1}$)

When pyrite (the sulfide mineral) is not present, the diffusive flux is simply expressed by Fick's first law:

$$F = D (C_1 - C_2) / dx \quad (2.4.6)$$

where

F = the flux of oxygen across the top boundary ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

The effective diffusivity coefficient, D_e , is estimated from equation (2.2.6.). The zero-order reaction rate constant is estimated from the biological and chemical reaction rate constants as:

$$R = 3.75 (R_1 + R_2) \frac{\alpha_p}{V_g} \quad (2.4.7)$$

where

R = zero-order reaction rate constant ($\text{mol.m}^{-3}.\text{mth}^{-1}$)

R_1 = biological reaction rate constant ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

R_2 = chemical reaction rate constant ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

α_p = pyrite surface area per unit volume tailings ($\text{m}^2.\text{m}^{-3}$)

V_g = volume of gas per unit volume of tailings ($\text{m}^3.\text{m}^{-3}$)

The derivations of R_1 and R_2 are presented in Section 2.3. The factor, 3.75, is a stoichiometric factor (mole O_2 consumed per mole pyrite oxidized).

2.4.3 Advection Transport

In water saturated soil the gaseous diffusivity is small. The major transport

route for oxygen is via infiltrating water. This advective flux however, is small relative to transport by gaseous diffusion in the unsaturated zone. It provides a boundary condition at the water table and can be expressed as:

$$F = V C_w K_H \quad (2.4.8)$$

where

C_w = the concentration of oxygen (in solution) at the air-water boundary (mol.m^{-3})

V = the rate of infiltration of water (m.mth^{-1})

K_H = Henry's Law Constant ($\text{m}^3.\text{m}^{-3}$)

Overall Mathematical Solution

Oxygen transport and oxygen consumption are described by coupling the various solutions at the appropriate boundaries. Different combinations of consumption in adjoining layers give different analytical solutions for each interface dependent upon the conditions involved. This results in 6 possible equations that can apply to the top boundary, 6 equations for intermediate boundaries and 3 equations for the bottom boundary. These equations are developed and presented in Appendix C, Section C.2.2.

The general equation that applies to all conditions has a linear algebraic form which in matrix notation, is:

$$\underline{A} \underline{C} = \underline{W} \quad (2.4.9)$$

where

$\underline{A}$ = the matrix of coefficients (m.mth^{-1})

$\underline{C}$ = the concentration of oxygen with depth (mol.m^{-3})

$\underline{W}$ = the loading term ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

A is an nxn matrix, and C and W are nx1 matrices. There are up to 3 coefficients in each row of A having a non zero value. The values of these coefficients change due to the 15 different conditions possible. The A matrix is tridiagonal with the dominant diagonal containing the A coefficients for the middle interface and the upper and lower diagonals containing the upper and lower interface coefficients respectively. The mathematical solution for C is found by simultaneous solution of the N equations where N equals the number of interfaces or layers.

2.5 Pyrite Oxidation Module

In the pyrite oxidation module the depletion of the pyrite content in the tailings is calculated. The effects of oxygen concentration, pyrite surface area and the kinetic rate constants are employed in the calculation of the overall reaction rate. Appendix D presents a detailed description of the pyrite oxidation module.

The overall reaction rate for pyrite oxidation can be expressed as:

$$\frac{dM}{dt} = -\frac{A_p}{V} (R_{1b} + R_2) \quad (2.5.1)$$

where

- M = moles of pyrite per unit volume of tailings (mol.m⁻³)
- R_{1b} = biological specific reaction rate per unit area of pyrite (mol.m⁻² mth⁻¹)
- R₂ = chemical specific reaction rate per unit area of pyrite (mol.m⁻² mth⁻¹)
- A_p = surface area of pyrite (m²)
- V = volume of tailings (m³)
- t = time (mth)



2.5.1 Rate Limitation due to Oxygen Concentration

The biological reaction rate constant defined above, R_{1b} , is effectively a "material" constant and is independent of oxygen concentration. The net biological oxidation rate is equal to this "material" constant times an oxygen factor. The limiting effect of oxygen on the biological specific reaction rate can be included in equation (2.5.1) by replacing the term R_1 with:

$$R_{1b} = R_1 \frac{P_{O_2}}{L_0 + P_{O_2}} \quad (2.5.2)$$

where

- P_{O_2} = partial pressure of oxygen (atm)
 L_0 = limiting oxygen partial pressure (atm)
 R_{1b} = oxygen influenced biological specific reaction rate
($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)

This equation includes the influences of oxygen concentration using a Monod type expression. It is essentially equivalent to the zero order and first order rate expressions used in the oxygen model: it has a value equivalent to the zero order constant (R_1) at high oxygen concentrations and equivalent to the first order rate constant $k_b = R_1/L_0$ at low oxygen concentrations where $L_0 = .01$.

The chemical term, R_2 in equation (2.5.1), incorporates a first order oxygen dependence:

$$R_2 = f_p k_c P_{O_2} \quad (2.5.3)$$

where:

- k_c = chemical rate constant ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1} \cdot \text{atm}^{-1}$)
 R_2 = chemical specific reaction rate ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)
 f_p = pH dependence factor

Oxygen dependence of pyrite oxidation upon the chemical and biological

kinetics results in a mixed dependence which is neither Monod nor first order. As indicated above, the biological component is much larger than the chemical component over much of the acidic pH range, the range of concern for this project. This allowed the simplifying assumption that the overall oxygen dependence is essentially a Monod expression. Subsequent inspection of this assumption involving analysis of calculated fluxes, showed that this assumption was justified.

2.5.2 Effect of Particle Size Distribution

As oxidation proceeds the surface area of individual pyrite particles decreases. The rate at which the pyrite particle "shrinks" due to dissolution by oxidation is given by the following expression:

$$\frac{dM}{dt} = -\left(\rho_p \frac{A_p}{V}\right) \frac{dr}{dt} \quad (2.5.4)$$

where:

ρ_p = moles of pyrite per volume of pyrite (mol.m^{-3})

r = average radius of pyrite particles (m)

V = volume of tailings (m^3)

A_p = total surface area of pyrite particles (m^2)

The expression assumes that the pyrite particles are spherical.

The overall rate of pyrite oxidation can be determined by combining equations (2.5.1) and (2.5.4):

$$\left(\frac{\rho_p}{V} A_p\right) \frac{dr}{dt} = \frac{A_p}{V} (R_{1b} + R_2) \quad (2.5.5)$$

or

$$\frac{dr}{dt} = \frac{R_t}{\rho_p} \quad (2.5.6)$$

where



R_t = overall specific reaction rate, (i.e. $R_{1b} + R_2$) ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

Integration of equation (2.5.6) by assuming that R_t is constant for the time period "0 to t" yields:

$$r = r_0 - \left(\frac{t R_t}{\rho_p} \right) \quad (2.5.7a)$$

$$r = r_0 - k_0 t \quad (2.5.7b)$$

where

r_0 = initial radius of particle (m)

k_0 = rate constant for oxidation (m.mth.^{-1})

Substitution of a term for the concentration of pyrite remaining, moles of pyrite per m^3 of tailings, as a function of surface area and time gives:

$$M_{r,t} = M_{r,0} \left(\frac{r - k_0 t}{r_0} \right)^3 \quad (2.5.8)$$

for $r \geq k_0 t$. The details are given in the Appendix.

The initial radii of pyrite grains in tailings however, are not of a uniform size, but have various sizes. The radii can be described by the following size distribution density function:

$$f(r) = \frac{x \alpha}{r_m} \left(\frac{r}{r_m} \right)^{\alpha-1} + \frac{y \beta}{r_m} \left(\frac{r}{r_m} \right)^{\beta-1} \quad (2.5.9)$$

where

$f(r)$ = size distribution density function

r_m = maximum radius of particles (m)

x, y, α, β = Pareto distribution function coefficients ($x + y = 1$)

Hence, the total mass of pyrite per volume of tailings at any 't' (M_t) is given by substituting equation (2.5.9) into equation (2.5.8) to give the following integral:

$$M_t = M_0 \int_0^{r_m} \left(\frac{r - k_0 t}{r_0} \right)^3 \left[x \alpha \left(\frac{r}{r_m} \right)^{\alpha-1} + y \beta \left(\frac{r}{r_m} \right)^{\beta-1} \right] \frac{dr}{r_m} \quad (2.5.10)$$

where

M_0 = initial pyrite concentration in moles per volume of tailings ($\text{mol} \cdot \text{m}^{-3}$).

Integrating the above expression results in the following polynomial expression:

$$M_t = \left[M_0 \left\{ 1 + a_1 \left(\frac{k_0 t}{r_m} \right)^\alpha + a_2 \left(\frac{k_0 t}{r_m} \right)^\beta + a_3 \left(\frac{k_0 t}{r_m} \right) + a_4 \left(\frac{k_0 t}{r_m} \right)^2 + a_5 \left(\frac{k_0 t}{r_m} \right)^3 \right\} \right] \quad (2.5.11)$$

where:

r_m = the initial maximum radius and $k_0 t \leq r_m$

$$a_1 = -x \left(1 - \frac{3\alpha}{\alpha-1} + \frac{3\alpha}{\alpha-2} - \frac{\alpha}{\alpha-3} \right)$$

$$a_2 = y \left(1 - \frac{3\beta}{\beta-1} + \frac{3\beta}{\beta-2} - \frac{\beta}{\beta-3} \right)$$

$$a_3 = \left(-\frac{3x\alpha}{\alpha-1} - \frac{3y\beta}{\beta-1} \right)$$



$$a_4 = \frac{3x\alpha}{\alpha-2} - \frac{3y\beta}{\beta-2}$$

$$a_5 = -\left(\frac{x\alpha}{\alpha-3} - \frac{y\beta}{\beta-3}\right)$$

Once the pyrite concentration has been determined, the relationship between surface area and volume of tailings can be calculated for any time by differentiating equation (2.5.11) to give:

$$\alpha_p = -\frac{M_0}{\rho_p r_m} \left[a_1 \alpha \left(\frac{k_0 t}{r_m} \right)^{\alpha-1} + a_2 \beta \left(\frac{k_0 t}{r_m} \right)^{\beta-1} \right. \\ \left. + a_3 + 2a_4 \left(\frac{k_0 t}{r_m} \right) + 3a_5 \left(\frac{k_0 t}{r_m} \right)^2 \right] \quad (2.5.12)$$

2.6 Solute Transport Module

In the solute transport module, the mass transport of aqueous species via percolating water, and a solids balance are determined. The particular algorithms employed in the calculations are a function of the presence or absence of various minerals such as calcite, gypsum and solids containing aluminum and iron.

The solute transport model assumes that water infiltrates vertically down through the unsaturated zone to the saturated zone in a plug flow manner. From the saturated zone, water flows horizontally to surface water or vertically downward depending upon the flow pathways. Two different types of dissolution affect the transport calculations: kinetically-controlled dissolution, and equilibrium controlled dissolution. Evidence available from the literature justifies the assumption that the dissolution of sericite and pyrite is kinetically controlled and that the dissolution of calcite, gypsum, basaluminite, and goethite is equilibrium controlled for the monthly-time-

scales of concern here (Beak, 1985).

For elements like potassium leached from sericite, the mass balance equation gives:

$$[K_i] = \frac{q_{i-1} [K_{i-1}] + f_K \cdot r_{ser} \cdot V_i}{q_i} \quad (2.6.1)$$

where

$[K_i]$, $[K_{i-1}]$ = the potassium concentration in water leaving layer i and layer $i-1$ respectively ($\text{mol}^{-1} \cdot \text{L}$)

q_i , q_{i-1} = the flow rate leaving layer i and layer $i-1$ respectively ($\text{L} \cdot \text{mth}^{-1}$)

r_{ser} = the sericite dissolution rate ($\text{mol sericite} \cdot \text{m}^{-3} \text{ tailings} \cdot \text{mth}^{-1}$)

f_K = the stoichiometry factor ($\text{mol potassium released} \cdot \text{mol}^{-1} \text{ sericite dissolved}$)

V_i = the volume of layer i (m^3)

The term $f_K \cdot r_{ser} \cdot V_i$ is the source of potassium from sericite dissolution ($\text{mol} \cdot \text{mth}^{-1}$).

A mass balance on sericite gives the following equation for the solid phase:

$$[Ser_t] = [Ser_{t-1}] - r_{ser} dt \quad (2.6.2)$$

where

$[Ser_t]$ = the mass inventory of sericite at time t ($\text{mol} \cdot \text{m}^{-3}$)

dt = the elapsed time between $t-1$ and t (mth)

These two equations are applicable for kinetically controlled dissolution. Equation (2.6.1) is applicable for aluminum provided that no other solid phase exists by substituting $[Al_T]$ for $[K]$ and the stoichiometric factor ($\text{mol Al released per mole sericite dissolved}$). Here $[Al_T]$ is the total aqueous concentration of Al, including solution complexes. Where basaluminite exists

or thermodynamic formation is predicted, then equilibrium conditions control the aqueous ionic concentration of aluminum $[Al_i]$. Basaluminite ($Al_4(SO_4)(OH)_{10}$) was used here to describe solubility controls for Al. This choice was based on the findings of Dubrovsky *et al.* (1985) for Nordic which suggested that this solid phase better describes the observed solution concentrations than does the $Al(OH)_3$ solid phase. In this case:

$$[Al_i] = \frac{1}{f_3} \left(\frac{10^{KBAS - 10pH}}{f_2 [SO_4^{2-}]} \right)^{0.25} \quad (2.6.3)$$

where

f_2, f_3 = activity coefficients for 2^+ and 3^+ sericite species

$[SO_4]$ = the solution sulfate concentration ($mol.L^{-1}$)

KBAS = the power for the basaluminite solubility constant.

Because the ionic concentration of aluminum is a function of pH and sulfate concentration, its value is simultaneously obtained with the solution of the equation for pH (see below).

For an element such as aluminum which dissolves and which may participate in formation of another solid, the solid's mass balance is:

$$[BAS]_t = [BAS]_{t-1} + (q_{i-1} [Al_T]_{i-1} + f_{Al} r_{ser} V_i - q_i [Al_T]_i) dt \quad (2.6.4)$$

where

$[BAS]_t$ = the basaluminite concentration ($mol.m^{-3}$)

f_{Al} = the aluminum sericite stoichiometry factor

$[Al_T]_{i-1}$ = the total aqueous aluminum concentration in layer $i-1$ ($mol.m^{-3}$)

For other elements such as Fe^{3+} , Ca^{2+} , SO_4^{2-} ; similar equations are used to solve for the aqueous concentrations and inventory, dependent upon whether or not a solid phase exists at equilibrium with solution. The only changes involved are formulation of the equilibrium relationship analogous to equation

(2.6.3) (Fe^{3+} with goethite; Ca^{2+} with gypsum and calcite; and SO_4^{2-} with gypsum) and of the presence or absence of a kinetic term in equation (2.6.4) (pyrite is the only other solid with a kinetic term).

The mass balance for Fe^{3+} and Fe^{2+} has an added complicating factor: in a net sense a portion of the pyrite oxidized forms Fe^{3+} while the remainder forms Fe^{2+} . This occurs because Fe^{3+} is formed by bacterial oxidation but is reduced to Fe^{2+} during the dissolution of pyrite. This results in a source for Fe^{3+} :

$$\text{Source}_{\text{Fe}3} = (0.02 + P_{\text{O}_2}^{1/2}) \cdot R_{\text{pyr}} \cdot V_i \quad (2.6.5)$$

and the source for Fe^{2+} :

$$\text{Source}_{\text{Fe}2} = \left(\frac{0.46 - P_{\text{O}_2}^{1/2}}{0.48} \right) \cdot R_{\text{pyr}} \cdot V_i \quad (2.6.6)$$

These are empirical relationships based on laboratory data.

Under reducing conditions ($P_{\text{O}_2} = 0$), pyrite can be dissolved by Fe^{3+} entering a tailings layer with infiltrating rainwater. The net overall reaction results in an additional source term for Fe^{2+} and a sink term for Fe^{3+} under reducing conditions. The equations are:

$$\begin{aligned} \text{Source}_{\text{Fe}2} &= -\text{Sink}_{\text{Fe}3} \\ &= -K_{\text{Fe}3} [\text{Fe}^{3+}]_T \frac{L_{\text{O}_2}}{L_{\text{O}_2} + P_{\text{O}_2}} \exp \left[\frac{-E_{a2}}{1.987} \left(\frac{1}{T} - \frac{1}{298} \right) \right] V_i \end{aligned} \quad (2.6.7)$$

where

$K_{\text{Fe}3}$ = the reaction rate constant (mth^{-1})

E_{a2} = the activation energy of the reaction (cal.mol^{-1})

T = the ground temperature ($^{\circ}\text{K}$).

2.7 Speciation Module

The main purpose of the speciation module is the calculation of the pH and the acid flux. The calculation of pH is based upon the principle of electroneutrality. For the ions of concern in this equation, it is:

$$10^{-\text{pH}} + 2[\text{Ca}^{2+}] + \text{ALUM} + \text{IRON} + 2[\text{Fe}^{2+}] + [\text{K}^+] = [\text{HCO}_3^-] + \text{SULF} + [\text{NO}_3^-] \quad (2.7.1)$$

where

$$\begin{aligned} \text{ALUM} = & (3 + 2 f_3 \text{CA1OH} 10^{\text{pH}}/f_2 + f_3 \text{CA1OH}_2 10^{2\text{pH}}/f_1 + \\ & + f_3 \text{CA1OH}_3 10^{3\text{pH}} + f_3 f_2 \text{CA1SO}_4 [\text{SO}_4^{2-}]/f_1) [\text{Al}^{3+}] \end{aligned} \quad (2.7.2)$$

$$\begin{aligned} \text{IRON} = & (3 + 2 f_3 \text{CFeOH} 10^{\text{pH}}/f_2 + f_3 \text{CFeOH}_2 10^{2\text{pH}}/f_1 + \\ & + f_3 \text{CFeOH}_3 10^{3\text{pH}} + f_3 f_2 \text{CFeSO}_4 [\text{SO}_4^{2-}]/f_1) [\text{Fe}^{3+}] \end{aligned} \quad (2.7.3)$$

$$\text{SULF} = (2 + f_2 10^{-\text{pH}}/(\text{CHSO}_4 f_1))[\text{SO}_4^{2-}] \quad (2.7.4)$$

where

CA1OH, CA1OH₂, CA1OH₃, CA1SO₄,

CFeOH, CF₂OH₂, CF₃OH₃, CF₄SO₄ = thermodynamic complexation constants

f₁, f₂ and f₃ = activity coefficients

All chemical concentrations refer to layer i whether or not explicitly 'subscripted with "i". The term 'ALUM', 'IRON', and 'SULF' refer to solution complexes of aluminum, iron and sulfate which have a charge. For 'ALUM' and 'IRON', the respective complexes in equation (2.7.2) and (2.7.3) are the 3+, (Al³⁺, Fe³⁺), 2+ (AlOH²⁺, FeOH²⁺), the 1+ (Al(OH)₂⁺, Fe(OH)₂⁺) and sulfate (AlSO₄⁺, FeSO₄⁺) complexes. For sulfate, equation (2.7.4), the respective species are SO₄²⁻ and HSO₄⁻.

The [Al³⁺] is estimated from the solubility constant and pH if the solid phase

is present, but from $[Al_T]$ (from solution mass balance) and pH if no solid phase is present. $[Fe^{3+}]$ is estimated similarly. $[Ca^{2+}]$ and $[SO_4^{2-}]$ are estimated from equilibrium considerations if gypsum is present and from solution mass balance if it is absent. If calcite is present, $[Ca^{2+}]$ is estimated from gypsum equilibria and $[HCO_3^-]$ is estimated from the following expression for tailings layers which are not fully saturated:

$$[HCO_3^-] = \frac{K_1}{K_H f_1 10^{-pH}} P_{CO_2} \quad (2.7.5)$$

K_1 = the dissociation constant for carbonic acid (mol.L⁻¹)

K_H = Henry's constant for carbon dioxide (atm.L.mol⁻¹)

P_{CO_2} = the partial pressure of carbon dioxide (atm)

$[HCO_3^-]$ = the bicarbonate concentration (mol.L⁻¹)

For saturated tailings layers,

$$[HCO_3^-] = \frac{K_1}{f_1 10^{-pH} + K_1} C_T \quad (2.7.6)$$

where

C_T = the total inorganic carbon concentration in solution, calculated by mass balance (mol.L⁻¹)

The pH is calculated by finding the root of equation (2.7.1) (i.e. where the L.H.S. equals the R.H.S.) using an iterative search technique.

The two routines, transport and speciation are solved simultaneously depending upon which solid phases are present. Generally solution mass balance calculations are first made, the pH estimated, and then the remaining mass balance calculations are made (for solid phases, and solution phases if a solid phase completely dissolves during a time step).

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3.0 MODEL VALIDATION

3.1 Introduction

In this section, values calculated for pH, aqueous and solid phase species concentrations, soil water contents, and gaseous compositions by RATAP are compared against data collected at the Nordic tailings site in Elliot Lake, Ontario. The predicted values are from a deterministic simulation of the tailings behaviour over a 20 year time period, equivalent to the age of the Nordic tailings area.

The input values employed in the deterministic simulation are the nominal values listed in Table 4.1. Some site specific soil parameters were used and are listed in Table 3.1. These input values are estimates of the characteristics of the Nordic tailings in 1968 because actual measurements on the tailings were not made at the time of the tailings placement.

Other than these few site specific values, none of the other input parameter values were changed. The emphasis in this chapter is on model validation, not calibration.

3.2 Description of Field Data

The field data of Smyth (1981), were sampled during August 1980 at the Nordic tailings impoundment located approximately 4 km east of Elliot Lake, Ontario. The Nordic tailings were deposited from 1957 to 1968 during the operation of the mine.

The data selected for comparison with model predictions are from sampling sites located about 0.75 km apart on the tailings, designated as T3 and T5 by Smyth (1981). Water table elevations are quite different at these locations. Location T5 consists predominantly of coarse grained tailings adjacent to the tailings discharge pipe. The depth of the water table at this location varies between 4 and 4.5 m. At T3 the tailings are predominantly slimes



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Table 3.1

SITE SPECIFIC PARAMETERS USED IN SIMULATION

Parameter	Value												
	Location T3							Location T5					
	Layer							Layer					
	1-6	7	8	9	10	11	12-15	16-17	18-21	1-13	14-21		
λ (unitless)	0.78	0.68	0.73	0.68	0.73	0.68	0.78	0.68	0.73	0.68	0.73		
H_e ($m^3 \cdot m^{-3}$)	-1.5	-1.1	-0.5	-1.1	-0.5	-1.1	-1.5	-1.1	-1.5	-1.1	-0.5		
n_r^* ($m^3 \cdot m^{-3}$)	0.30	0.15	0.20	0.15	0.20	0.15	0.3	0.15	0.3	0.10	0.13		
n_t ($m^3 \cdot m^{-3}$)	0.6	0.5	0.55	0.5	0.55	0.5	0.6	0.5	0.6	0.40	0.45		
dx (m)				0.325							0.20		
Z_{water} (m)				6.25							4.0		
X_{pyr} (%)				6.00							11.0		

Note

* Representative of slimes.

Reference

Based on data from Smyth (1981)

material. At this location the water table depth varies between 6.0 and 6.5 m.

The field data include information on the tailings solids and on the porewater. Core samples were collected in the zone above the water table. Information on the solid phase includes a description of grain-size characteristics, bulk density, pyrite content and carbonate content. Liquid phase data includes water content, pH and other chemical data. In addition the oxygen concentration in the gas-filled pores was measured at various depths.

The grain size distribution measured from field samples are not used in the model directly. These data were used, however, to provide estimates of the air entry value (height of capillary fringe) and residual water content, both of which are input parameters. No attempt was made to "fit" the parameter values to the data precisely, but the limits of these values for sand-and silt- sized material were used (i.e. $h_e = -0.5\text{m}$ for sand; $h_e = -1.5\text{m}$ for silt). In fact, only four site-specific parameters were used in the model. They are the depth of the water table (Z), and parameters which determine the moisture content (h_e , n_r and n_t).

Porewater data were measured by Smyth (1981) in August 1980 and May 1981. These data are fairly variable. The temporal trends were not always consistent with expected temporal trends. In addition, an electroneutrality was not always obtained for porewater chemistry. Some samples, especially those with high iron and sulphate concentrations in the range of equivalents per million balance (epm), had an imbalance of greater than 30%. This suggests that a disagreement between model calculations and observations of up to 30% can be expected due to sampling and analytical variability.

It was also noted during oxygen sampling that the tailings surface was affected by dessication cracking. This feature appears to have resulted in near atmospheric levels of oxygen down to about 0.5 meters depth at site T3 (see Figure 3.16). This surface cracking represents a condition affecting



oxygen transport which was not incorporated in the validation modelling exercise.

3.3 Comparison of Model Calculations and Observations for pH

Figures 3.1 and 3.2 present comparisons of the observed and predicted pH values for locations T3 and T5, respectively. Model predictions generally agree with observations within one pH unit. The predictions also agree with the trend of observations, but generally exhibit sharper gradients than were observed in the field. The apparent differences may be due to the fact that the model structure assumes the complete absence of a particular buffering system under equilibrium conditions, whereas the field data suggests that porewater is partially influenced by such a solid phase. Such solid phases would influence porewater where dissolution of the residual solid is kinetically rather than equilibrium controlled.

In the slime tailings (Figure 3.1) the predicted results are in very good agreement with those observed. The model's high pH value for the shallow depth of 0.3m occurs because pyrite is predicted to be depleted at this depth. The slight overestimation of the pH at depths greater than approximately 3.5 m may have resulted from the model employing inappropriate values for the partial pressure of carbon dioxide.

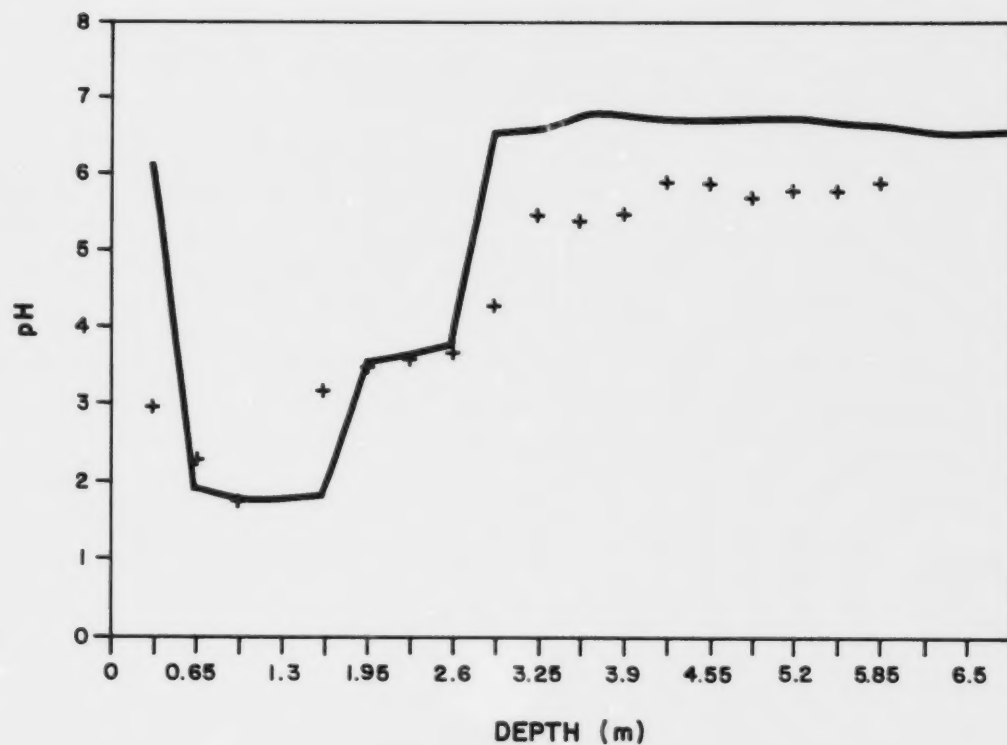
In coarse tailings (Figure 3.2), the model more closely predicts the pH. The model does not however, predict the gradual pH change observed between 1.8 to 3 m. The sharp change predicted by the model results from its predicted step-wise absence and presence of basaluminite with depth.

3.4 Prediction of Aqueous Phase Species Concentrations

Sulphate

Figures 3.3 and 3.4 present the predicted and observed concentrations of

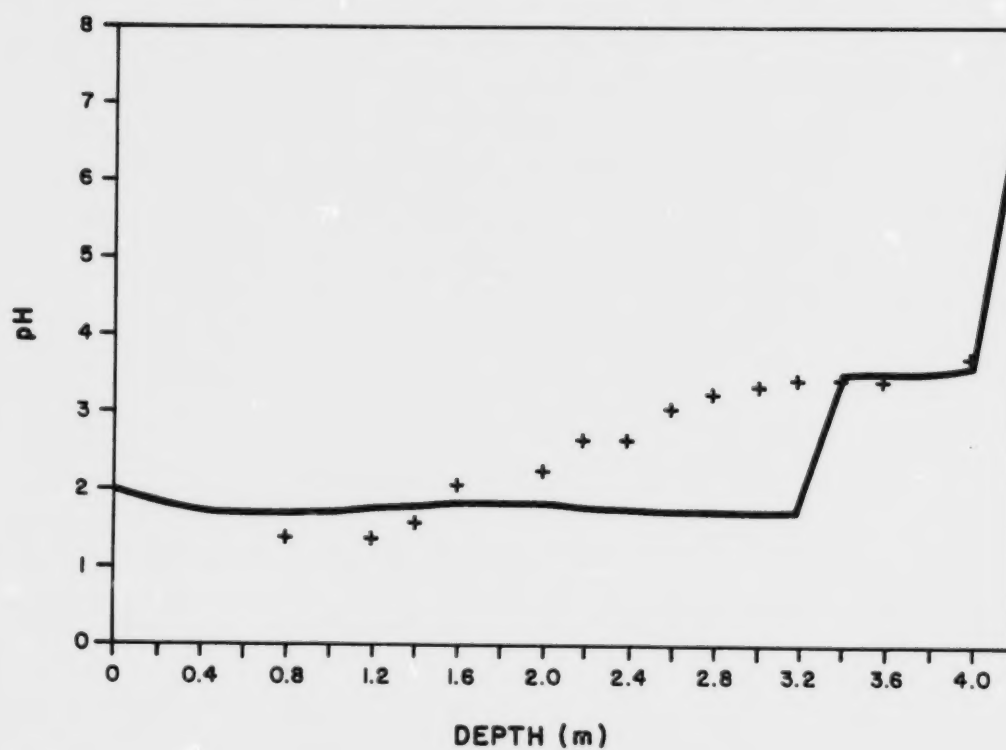
FIGURE 3.1
MODEL vs. FIELD pH VALUES
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
- + FIELD RESULTS OF SMYTH (1981)

FIGURE 3.2
MODEL vs. FIELD pH VALUES
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
- + FIELD RESULTS OF SMYTH (1961)

sulphate. At both sites the predicted sulphate concentrations (see Figure 3.3 for slime and Figure 3.4 for coarse tailings) are in very good agreement with field observations. The reason for the slightly high prediction for sulphate concentration at site T3 is unclear. It relates to a slightly excessive rate of pyrite oxidation, a phenomenon however which is not observed in the oxygen calculations (see Figure 3.16).

Calcium

Figures 3.5 and 3.6 present the predicted and observed aqueous concentrations of calcium for the slime and coarse tailings. Model predictions for calcium concentration are slightly low at both locations. This could be explained by gypsum equilibrium if predicted sulphate values were high. Predicted sulphate values are slightly high for the fine tailings (T3) but are in good agreement for the coarse tailings (T5). The predicted low calcium concentration at shallow depth (0.1 m) for site T5 is caused by the model predicting the absence of gypsum. The field data were not adequate however to confirm this point.

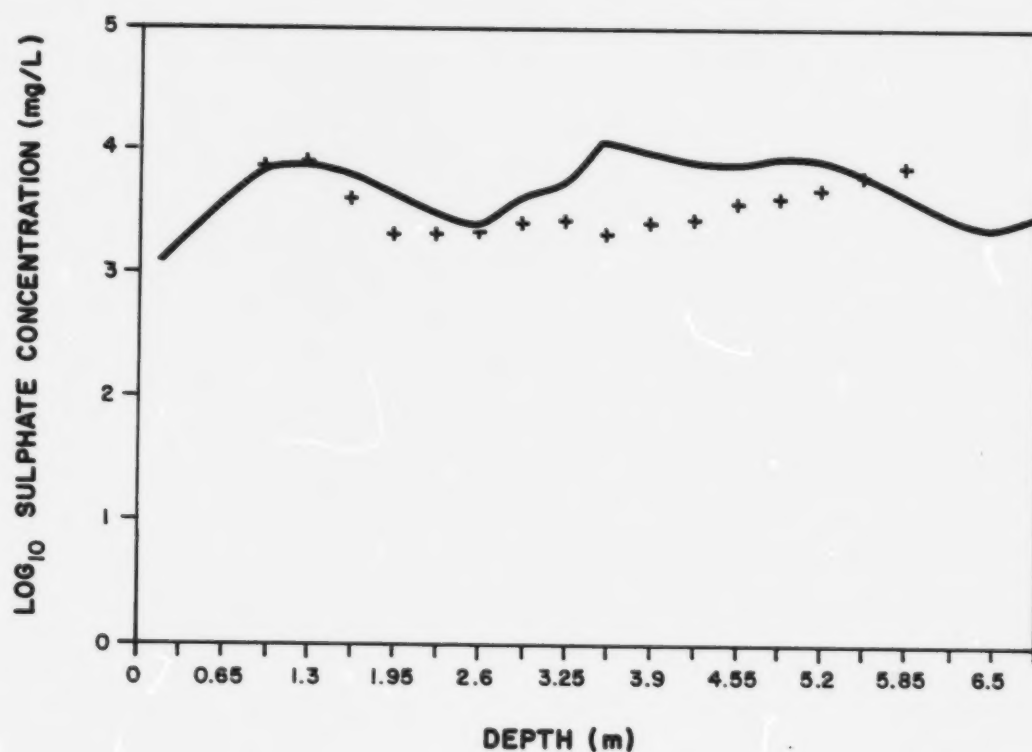
Aluminum

Figures 3.7 and 3.8 present the aqueous aluminum concentrations for T3 and T5, respectively. The high aluminum levels predicted by the model are associated with calcite being absent and basaluminite being present. For T3 the maximum aluminum concentrations are approximately 2 m deeper than the observed values. This suggests that the aluminum depletion rate predicted by the model was too high for the Nordic tailings. The aluminum concentrations are also high given the range of observed aluminum concentrations.

At T5, the model underestimates the aluminum concentration for most of the unsaturated zone (depths of 0.0 to 3.0 m). The low predicted aluminum concentrations are attributable to the fact that solid phase aluminum is absent at these depths. However, the model does predict the observed aluminum



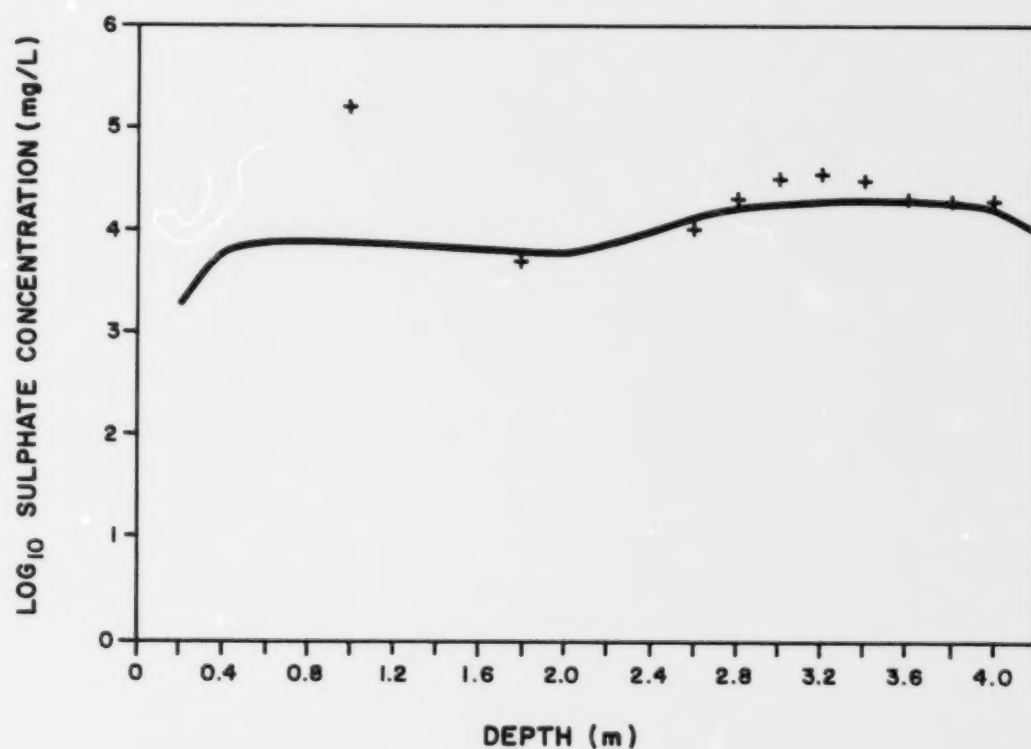
FIGURE 3.3
MODEL vs. FIELD SULPHATE CONCENTRATIONS
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

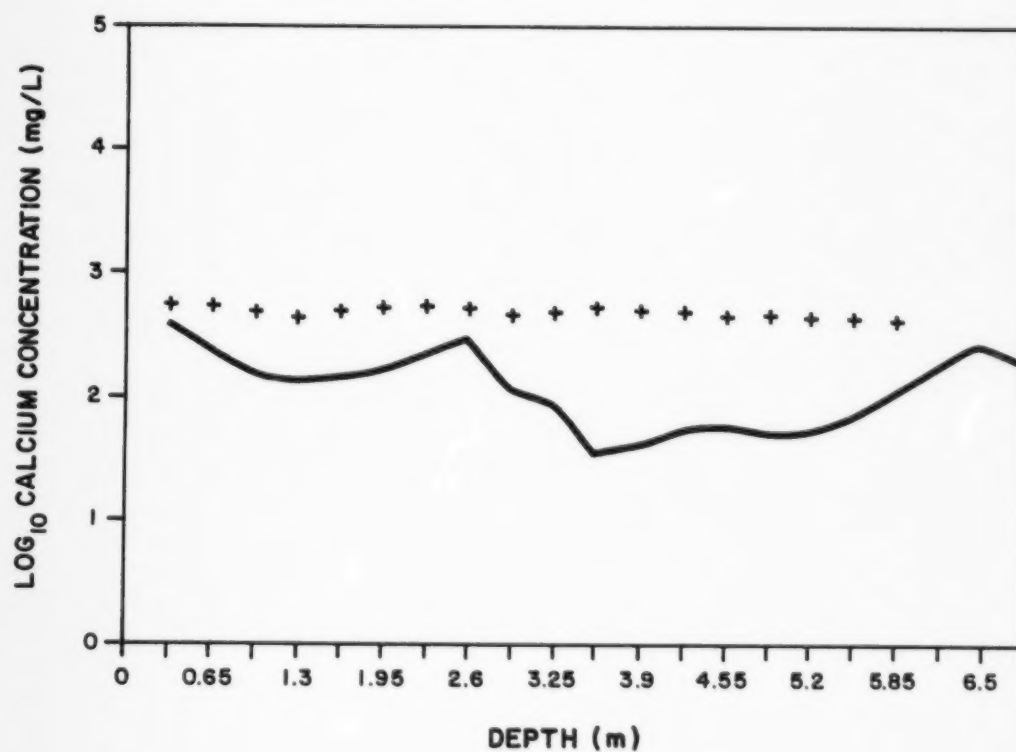
FIGURE 3.4
MODEL vs. FIELD SULPHATE CONCENTRATIONS
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

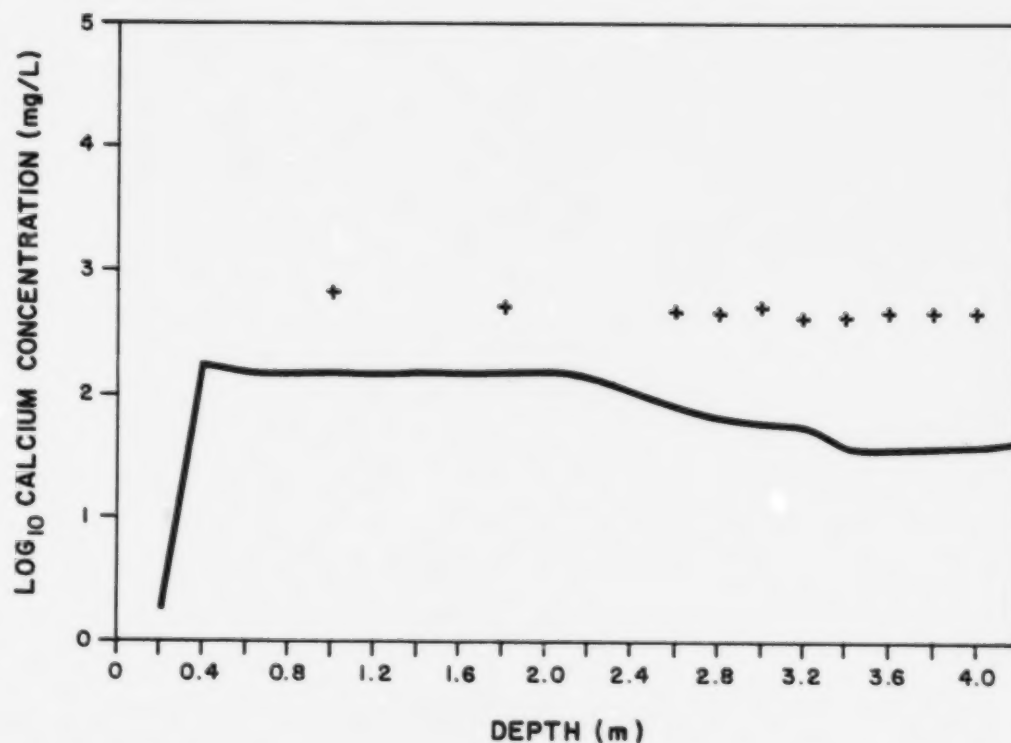
FIGURE 3.5
MODEL vs. FIELD CALCIUM CONCENTRATIONS
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

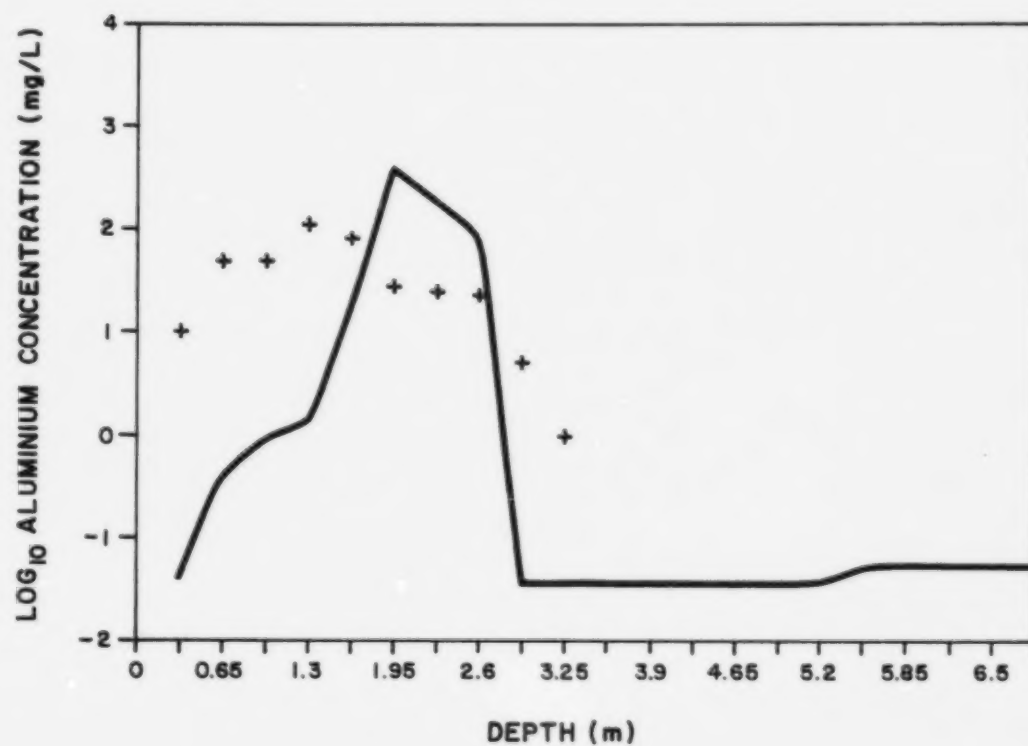
FIGURE 3.6
MODEL vs. FIELD CALCIUM CONCENTRATIONS
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

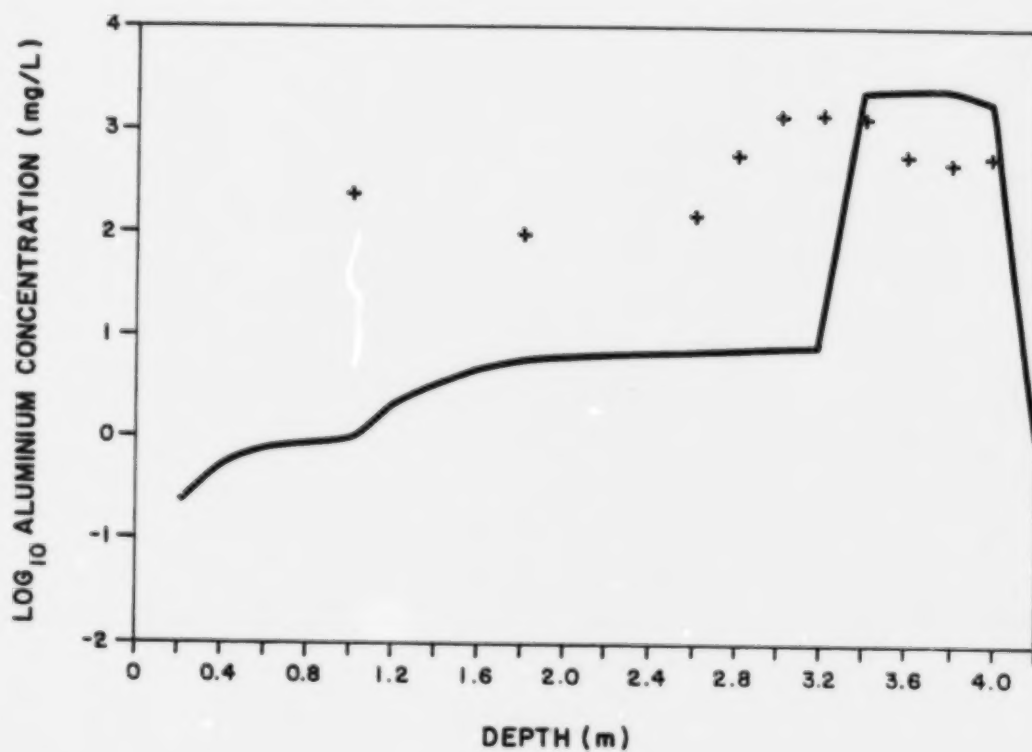
FIGURE 3.7
MODEL vs. FIELD ALUMINIUM CONCENTRATIONS
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

FIGURE 3.8
MODEL vs. FIELD ALUMINIUM CONCENTRATIONS
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

concentrations when it calculates that the aluminum solid is still present (depths of 3 to 4 m).

It is concluded that aluminum chemistry involves more complex kinetic and/or equilibrium conditions than those used in this model .

Iron

The predicted and observed aqueous concentrations of iron, Fe_{total} , are presented in Figure 3.9 and 3.10. The models' predictions are in very good agreement with the field data. The low iron concentration predicted for the shallow depth of 0.3 m, occurs because pyrite is predicted to be depleted at this depth.

3.5 Solid Phase Species Concentrations

Pyrite

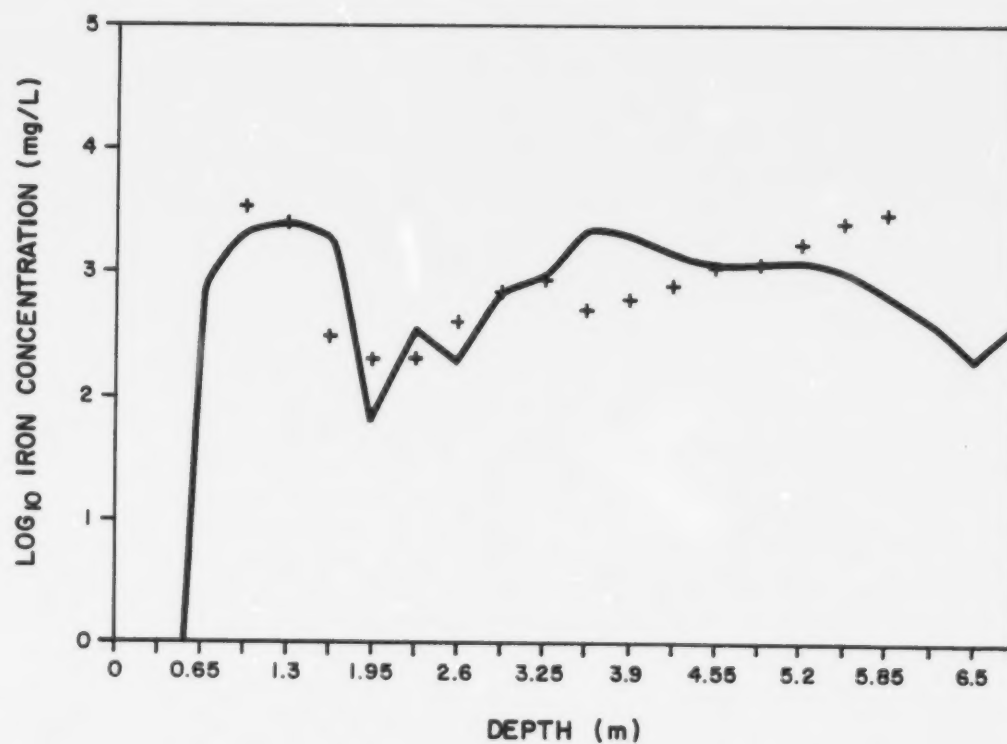
The depletion of pyrite as a function of depth is presented in Figures 3.11 and 3.12. The initial pyrite content assumed to be present at locations T3 and T5 was 6% and 11%, respectively.

At T3 the predicted and observed results are in good agreement throughout the profile; especially near the tailings surface where small amounts of pyrite remain. At T5 the predicted weight percentage of pyrite is also consistent with the field observations. At both T3 and T5, The predicted and observed results indicate that a substantial amount of pyrite remains throughout the full depth of the profile.

Calcite

At T3, the field data indicates that calcite has been depleted to a depth of approximately 3.6 m. This is in good agreement with the models prediction of

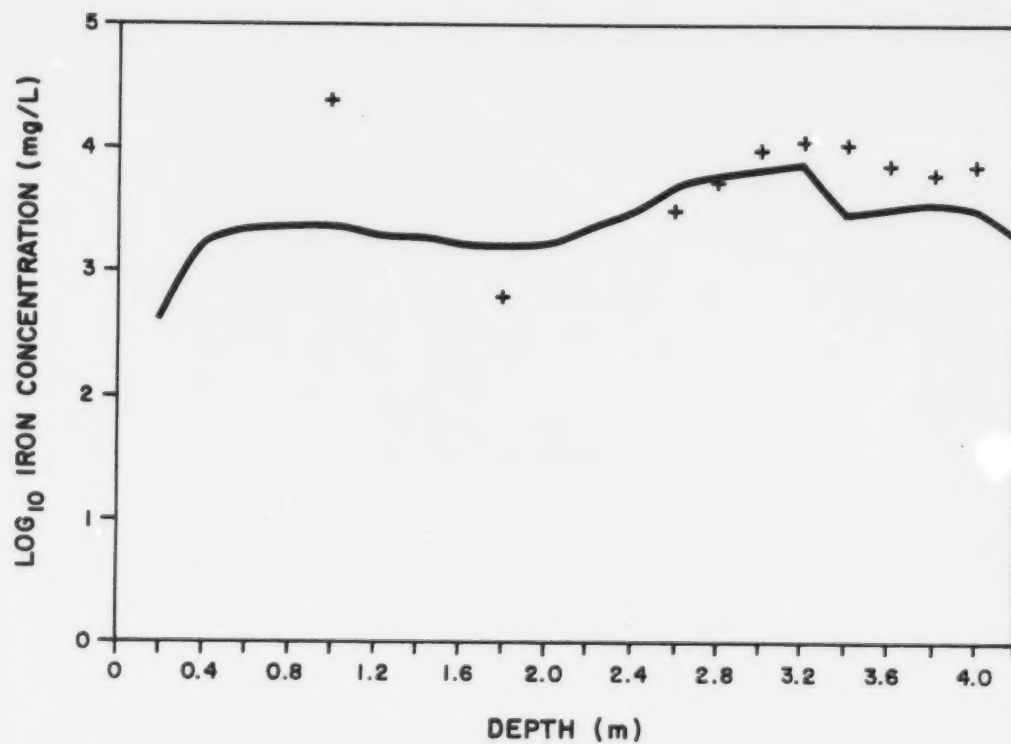
FIGURE 3.9
MODEL vs. FIELD IRON CONCENTRATIONS
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

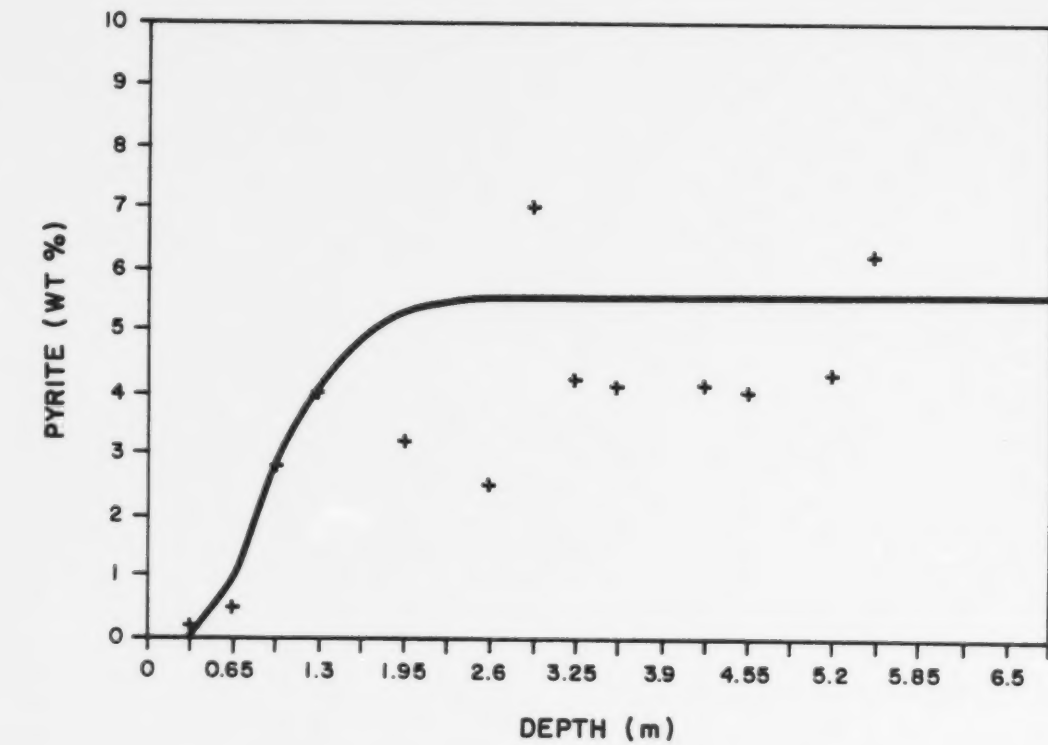
FIGURE 3.10
MODEL vs. FIELD IRON CONCENTRATIONS
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

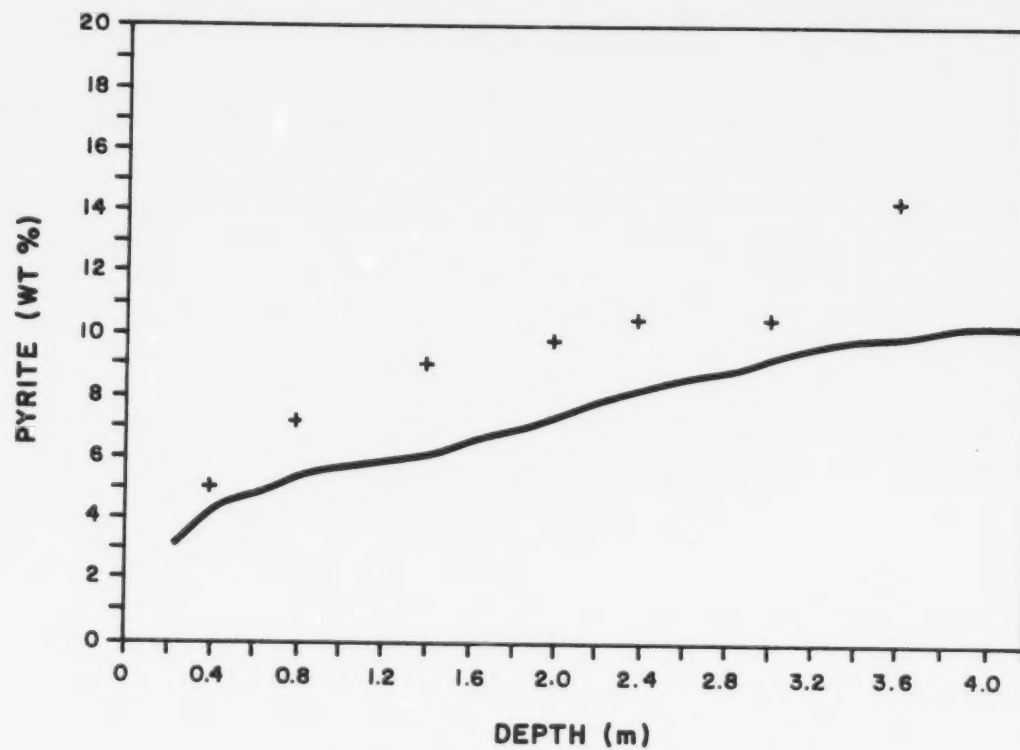
FIGURE 3.II
MODEL vs. FIELD PYRITE CONTENT
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

FIGURE 3.12
MODEL vs. FIELD PYRITE CONTENT
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

calcite depletion to a depth of 3.9 m (see Figure 3.13). At T5 both the model and field data indicate that calcite has been depleted to a depth of 4 m T5, the depth of the water table.

3.6 Water Content

Figures 3.14 and 3.15 present the predicted and observed water contents for the month of August. The model underpredicts the water contents at both sites, especially T3. The underprediction results from the models use of air entry values which were too low. Slime sized tailings may have air entry values that are much greater than those used in the model. In addition, non-equilibrium hydraulic conditions that are not readily predicted are quite common in heterogeneous layered porous media like the tailings.

3.7 Gas Composition

Figures 3.16 and 3.17 present predicted and observed oxygen profiles, for the two locations. In both cases there is reasonably good agreement between the observed and predicted values. At site T5 the model appears, however, to underpredict the steep oxygen gradient over the first meter depth. The observed steep oxygen profiles are the result of high water contents (representing low D_e values) which were underpredicted by the model. A more precise water content model based upon actual data should improve model calculations.

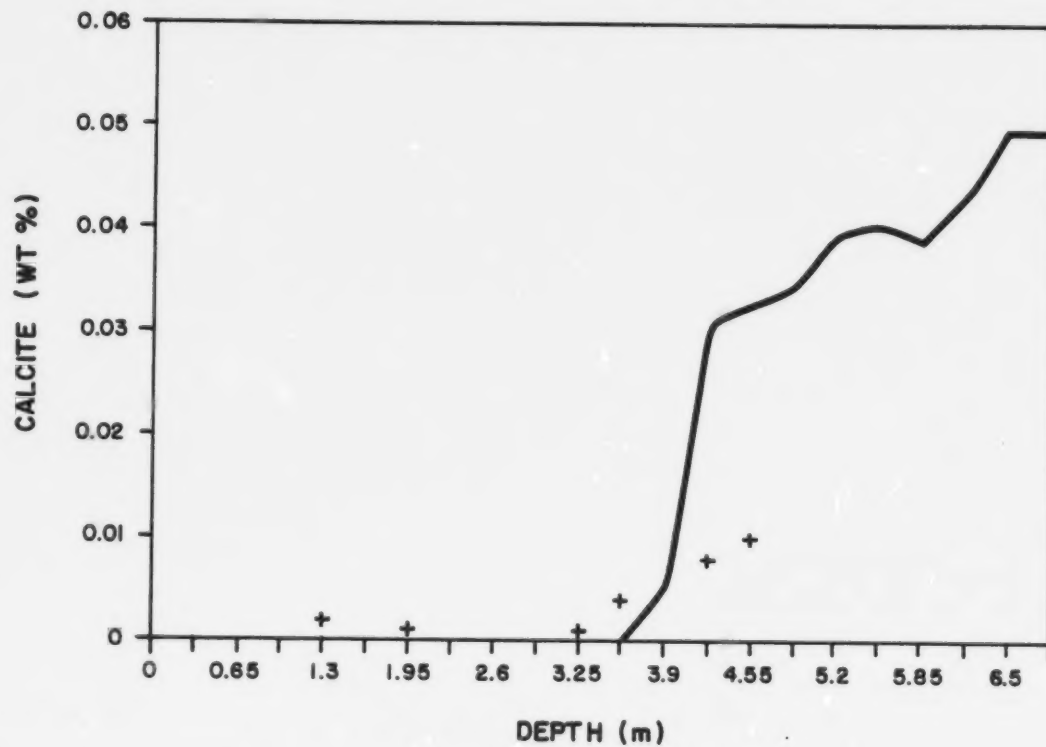
The field observations for oxygen indicate a residual of approximately 0.02 atm. at depths greater than 2 m. These results are most likely artifacts resulting from the use of inappropriate sampling techniques for tailings at low oxygen concentrations.

3.8 Summary

Model predictions have been compared with field observation for two sites at the Nordic tailings. Initial conditions for parameters such as moisture



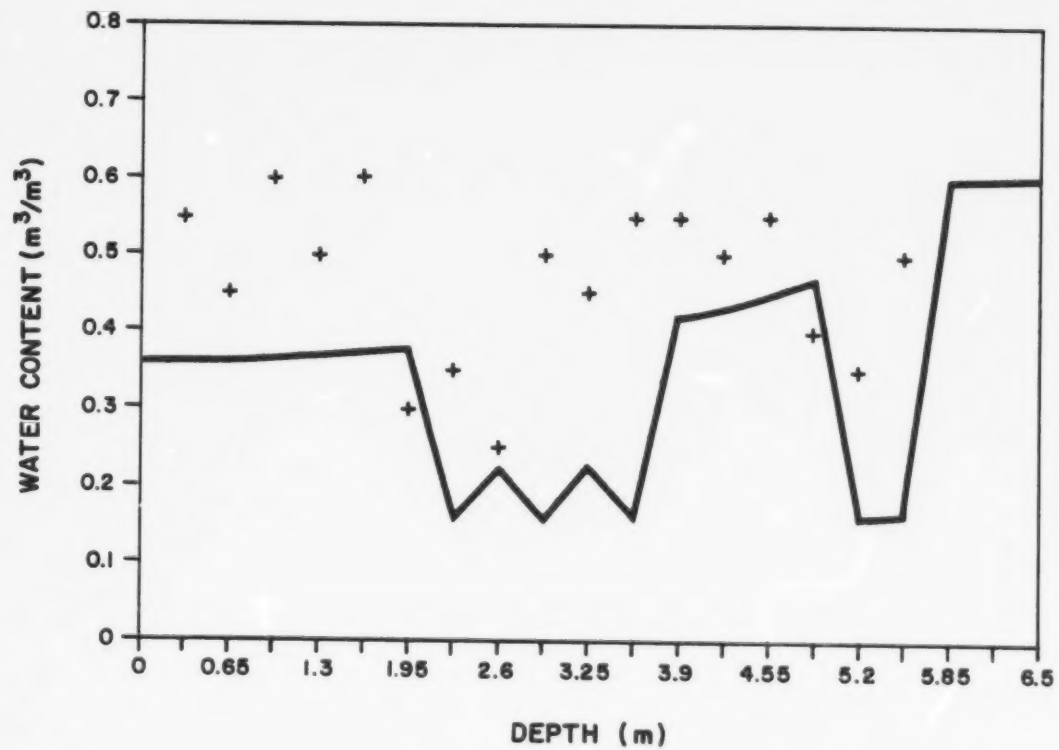
FIGURE 3.13
MODEL vs. FIELD CALCITE CONTENT
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

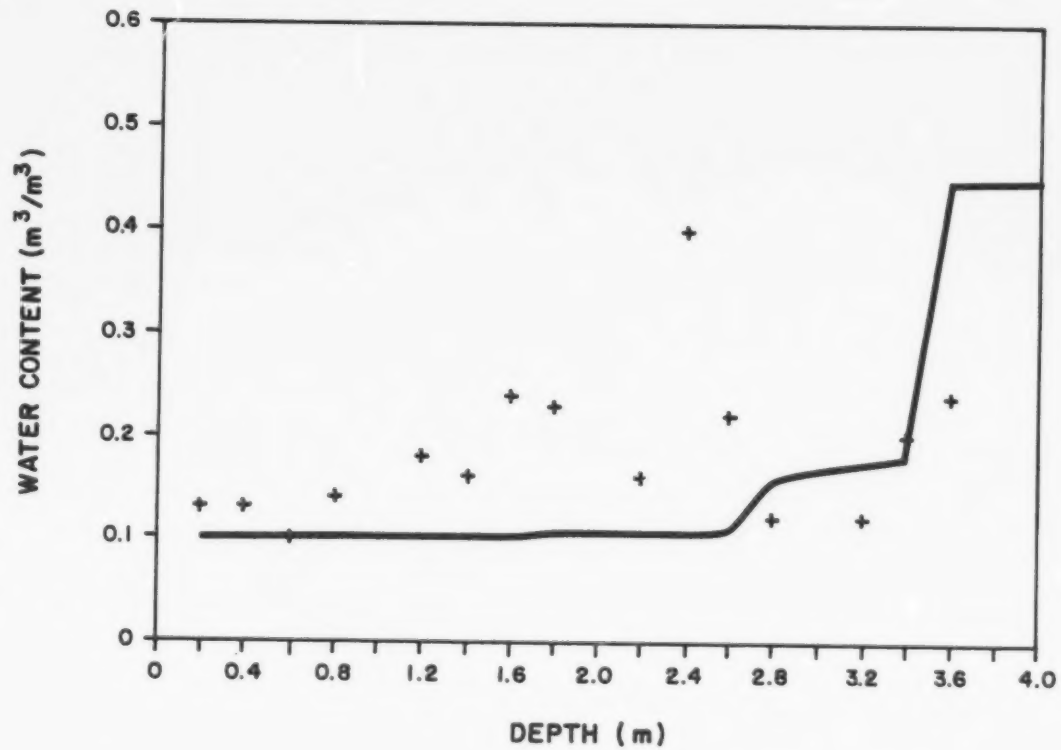
FIGURE 3.14
MODEL vs. FIELD WATER CONTENT
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

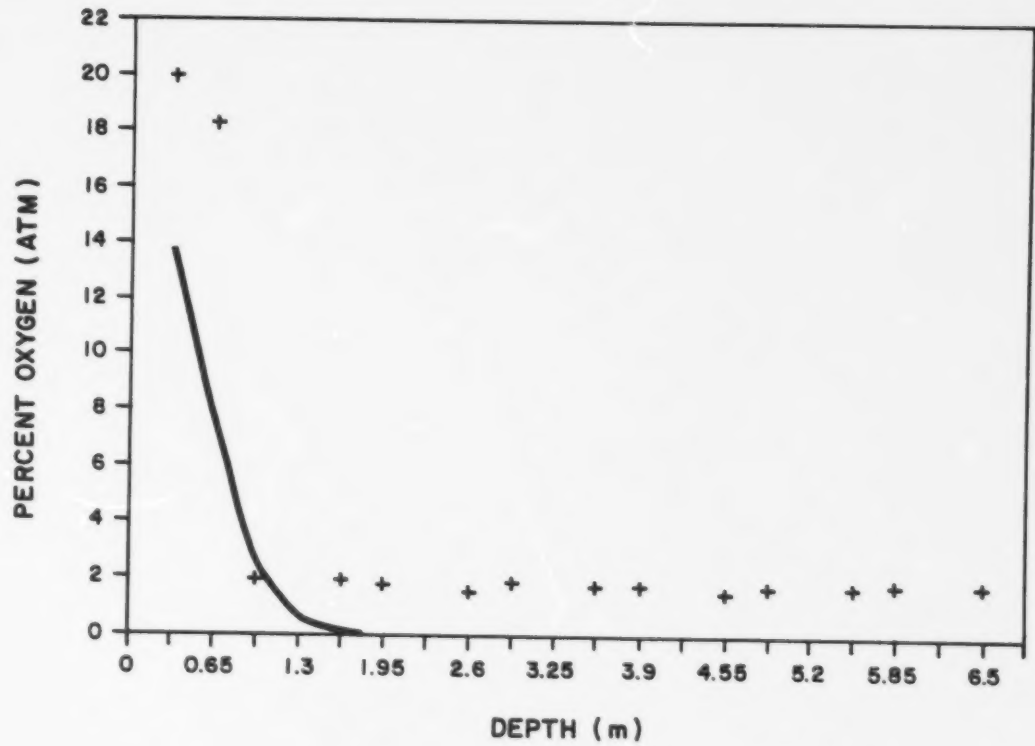
FIGURE 3.15
MODEL vs. FIELD WATER CONTENT
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

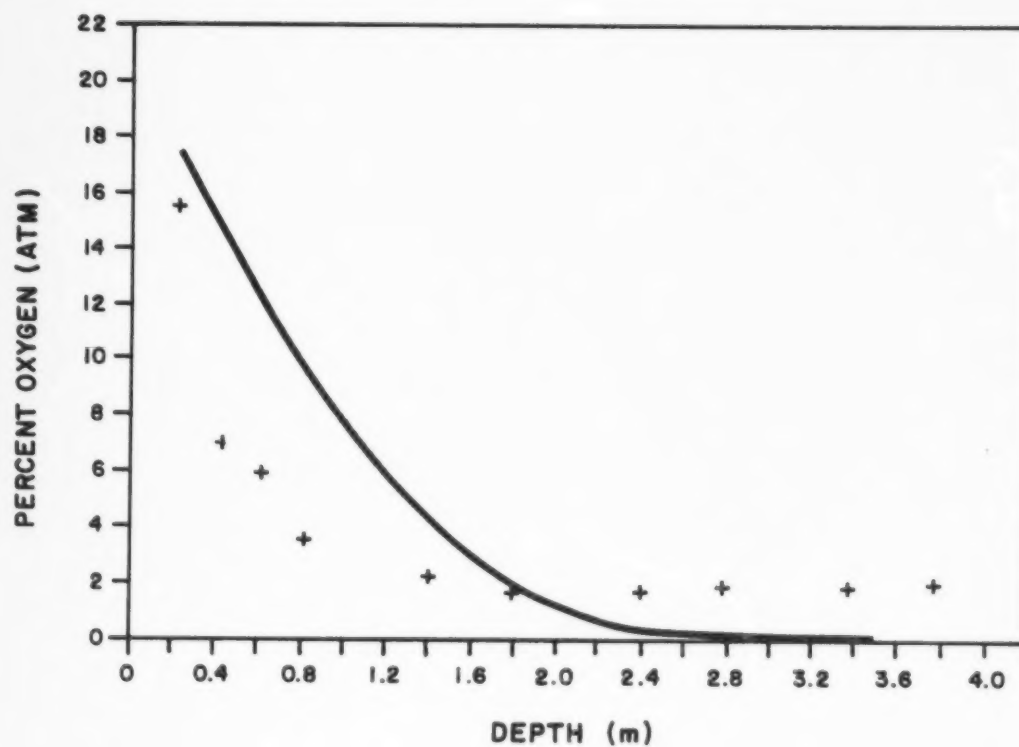
FIGURE 3.16
MODEL vs. FIELD OXYGEN VALUES
FOR T3



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

FIGURE 3.17
MODEL vs. FIELD OXYGEN VALUES
FOR T5



LEGEND:

- MODEL PREDICTED RESULTS
+ FIELD RESULTS OF SMYTH (1981)

content and pyrite content were estimated due to the lack of measurement when the tailings were first placed 20 years ago. Other input parameters were estimated based upon literature data. Overall, reasonably good agreement was obtained between the model predictions and the field observation for several pore water and solid phase parameters. This agreement provides substantial confidence in the ability of the model to calculate the limits of acid generation, particularly in light of unknowns related to initial inventories of the tailings.

The following represents specific comments on the models ability to predict specific parameters at the Nordic tailings site.

- 1- The model is able to predict the sulphate and iron concentration at all depths of a tailings site in a reasonable fashion.
- 2- The model overpredicts the rate of aluminum dissolution. This statement is supported by the underestimation of pH and aluminum concentrations at shallow depths.
- 3- The model is able to predict the depletion front of calcite but slightly underpredicts the dissolved calcium concentration.
- 4- The calculated pH values closely parallel the observed levels over most of the depth suggesting that the major chemical elements and buffering systems controlling pH and acidity are adequately represented in the model.
- 5- The predicted oxygen gradients are not as large as those observed. This results from the empirical moisture content model underpredicting the water content.



4.0 MODEL PREDICTIONS

4.1 Introduction

The primary objective of this study is to estimate the upper and lower limits of the rate and quantity of acid generation by the bacterially-assisted oxidation of pyrite and other sulfide minerals present in uranium mill tailings. In this section of the report the variability of the pyrite oxidation rate and the acid flux is examined for sulphidic uranium tailings characteristic of the Elliot Lake tailings with a water table depth of 2.0 m. Also presented is a sensitivity analysis. The sensitivity of the magnitude of the model outputs to changes in the magnitudes of the input parameters was assessed to delineate those parameters which have the greatest influence on the model predictions. The results of these analyses are discussed in the following sections.

Calculations of acid flux are presented for a standard case and using a probabilistic simulation. The rate and quantity of acid generation, predicted with the deterministic analysis, use nominal values of the input parameters in the RATAP code. The probabilistic simulation takes into account the expected range of uncertainty in the input parameters.

For the deterministic run, the generic tailings site was simulated for a 50 year period. From this simulation, predictions made by the model were extracted and are presented for two particular years (when the pH was controlled by basaluminite and ferric hydroxide, and when the pH was controlled only by ferric hydroxide) and two particular layers. Predictions presented include the rate of pyrite oxidation (Section 4.3) and the acid flux (Section 4.4).

The definition of acid flux employed in this study is:

$$\text{Acid} = (2 [\text{SO}_4^{2-}] + [\text{HCO}_3^-] - 2 [\text{Ca}^{2+}] - [\text{K}^+]) \frac{V_r}{A_x} \quad (4.1.1)$$

where

Acid = monthly acid flux ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

V_r = infiltration rate of precipitation into the tailings ($\text{m}^3.\text{mth}^{-1}$)

A_x = cross sectional area of the tailings (m^2)

[] = concentration of SO_4^{2-} , HCO_3^- , Ca^{2+} and K^+ ions in the tailings porewater (mol.m^{-3})

This accounts for all H^+ produced by pyrite oxidation less that consumed by calcite dissolution. The acid flux is defined in this project in terms of proton (H^+) equivalents. Hence one mole equals one equivalent, the actual units of equation 4.1.1.

Acid flux is also calculated as an annual flux as the summation of the 12 monthly acid flux values for a particular layer. In addition, the cumulative acid flux overtime is calculated; this equals the total acid generated from time zero to the end of the simulation period.

4.2 Input Parameter Distributions

A listing of the input parameters incorporated in the RATAP code and their nominal and probabilistic values are presented in Table 4.1. A total of 173 input parameters are employed in the detailed multi-component model discussed in the appendices. For the generic sulphide uranium tailings considered in this study, the parameters are assigned the following types of probability distributions: normal (22); triangular (64); uniform (29); lognormal (5); and constant (53). The number of parameters is based on the tailings profile being divided into twenty-two layers, and would be less if fewer layers were specified. The total number of input parameters for only one layer system equals 68. Detailed descriptions of the parameters and their distributions are presented in the appropriate appendices.

Table 4.1

MODEL INPUT PARAMETERS

Model Symbol	Parameter Description	Units	Nominal Value	Probability Distribution	Computer Symbol
1. Initial Inventory Module					
A_0	empirical temperature coefficient	(°K)	20	C(20)	AO
d	dampening depth	(m)	2.0	C(2.0)	D
h_e^*	air entry value	(m)	-0.5	T(-1.5, -0.5, -0.05)	HE
L	phase-shift constant	(unitless)	0.1	C(0.1)	COEFF
n_r^*	residual water content	($m^3_w \cdot m^{-3}_{tail}$)	0.08	N(0.08, 0.01, 0.05, 0.11)	NR(i)
n_t^*	porosity	($m^3_{void} \cdot m^{-3}_{tail}$)	0.50	T(0.45, 0.50, 0.55)	NT(i)
ρ_t	bulk density of the tailings	($kg \cdot m^{-3}$)	1300	C(1300)	BD
T_m	yearly mean temperature	(°K)	283	C(283)	TAVG
x_{pyr}	mass fraction of pyrite	($g \cdot g^{-1}$)	0.06	U(0.048, 0.072)	XPYR
x_{gyp}	mass fraction of gypsum	($g \cdot g^{-1}$)	0.05	U(0.04, 0.06)	XGYP
x_{FeOOH}	mass fraction of ferric hydroxide	($g \cdot g^{-1}$)	0.0041	U(0.0025, 0.0057)	XFE00H
x_{AlOH3}	mass fraction of basaluminite	($g \cdot g^{-1}$)	0.0023	U(0.0014, 0.0032)	XALOH3
x_{Ser}	mass fraction of sericite	($g \cdot g^{-1}$)	0.136	U(0.11, 0.16)	XSER
x_{cal}	mass fraction of calcite	($g \cdot g^{-1}$)	0.0005	U(0.000, 0.001)	XCAL
λ^*	soil coefficient for moisture content	(unitless)	0.73	U(0.68, 0.78)	LAMDA
2. Kinetics Module					
E_a	biological energy of activation	($cal \cdot mol^{-1}$)	11,700	T(10000, 11700, 16300)	EA1
E_{ac}	chemical energy of activation	($cal \cdot mol^{-1}$)	13,300	C(13,000)	EA2
k_c	chemical rate constant	($mol \cdot m^{-2} \cdot mth^{-1} \cdot atm$)	2.3×10^6	T(1.18×10^5 , 2.3×10^6 , 4.72×10^7)	KCONST
L_p	limiting phosphorus conc.	($mol \cdot m^{-3}$)	1.29×10^{-3}	C(1.29×10^{-3})	LP
P_{CO_2}	partial pressure of carbon dioxide	(%atm)	3.2×10^{-4}	C(3.2×10^{-4})	PCO2(i, t)
μ_{max}	maximum specific growth rate	(mth^{-1})	13.0	U(11.5, 14.5)	UMAX
x_p	biomass per surface area of pyrite	($g \cdot m^{-2}$)	1.6×10^{-3}	LW(1.6×10^{-3} , 1.7, 3.2×10^{-4} , 7.8×10^{-3})	XP
$Y_{x/s}$	biomass yield constant	($g \cdot mol^{-1}$)	3.2	T(2.5, 3.2, 4.2)	YXS

Table 4.1 (continued)

Model Symbol	Parameter Description	Units	Nominal Value	Probability Distribution	Computer Symbol
3. Oxygen Transport Module					
dx*	thickness of each layer	(m)	0.20	C(0.20)	DX
L	number of layers	(unitless)	22	C(22)	L
L _s	layers to saturated zone	(unitless)	21	C(21)	LS
K _H	Henry's Law constant for oxygen	(L.m ³)	23.6	C(23.6)	HENRY
Z	depth to water table	(m)	3.0	C(3.0)	ZWATER
4. Pyrite Oxidation Module					
L _o	limiting oxygen concentration	(atm)	0.01	C(0.01)	L02
p _p	molar density of pyrite	(mol.m ⁻³)	41670	C(41670)	DP
r _m	maximum radius	(m)	1.25x10 ⁻⁴	C(1.25x10 ⁻⁴)	RMAX
x	Paretto Coefficient	unitless	2	C(2)	A1
y	Paretto coefficient	unitless	-1	C(-1)	B1
a	empirical parameter for particle distribution	unitless	0.9	C(0.9)	AL
β	empirical parameter for particle distribution	unitless	1.8	C(1.8)	BE
5. Solute Transport Module					
Vr	infiltration rate for each month (i.e. for January m = 1; June, m = 6)	(m.mth ⁻¹)	m=1 0.005 2 0.005 3 0.005 4 0.090 5 0.070 6 0.030 7 0.020 8 0.030 9 0.050 10 0.050 11 0.040 12 0.005	T(0.001,0.005,0.01) T(0.001,0.005,0.01) T(0.001,0.005,0.01) T(0.018,0.09,0.18) T(0.014,0.07,0.14) T(0.006,0.03,0.06) T(0.004,0.02,0.04) T(0.006,0.03,0.06) T(0.01,0.05,0.1) T(0.01,0.05,0.1) T(0.008,0.04,0.08) T(0.001,0.005,0.01)	VR(i,m)
6. Aqueous Speciation Module					
f _{ALOH}	empirical coefficient for aluminum convergence	(unitless)	0.075	T(0.01,0.075,0.6)	FALOH
CHS04	T.S. constant for HSO ₄	(mol.L ⁻¹) ⁻¹	1.26E-2	C(1.26x10 ⁻²)	CHS04
CCAS04	T.S. constant for CASO ₄	(mol.L ⁻¹) ⁻¹	316.23	C(316.23)	CCAS04
CALS04	T.S. constant for ALSO ₄	(mol.L ⁻¹) ⁻¹	1047.13	C(1047.13)	CALS04
CFE0H	T.S. constant for FE0H	(mol.L ⁻¹) ⁻¹	6.46x10 ⁻³	C(6.46x10 ⁻³)	CFE0H

Table 4.1 (continued)

Model Symbol	Parameter Description	Units	Nominal Value	Probability Distribution	Computer Symbol
CFE0H2	T.S. constant for FE(OH) ₂	(mol.L ⁻¹) ⁻²	2.14x10 ⁻⁶	C(2.14x10 ⁻⁶)	CFE0H2
CFES04	T.S. constant for FES0 ₄	(mol.L ⁻¹) ⁻¹	8317.64	C(8317.64)	CFES04
CFE0H3	T.S. constant for FE(OH) ₃	(mol.L ⁻¹) ⁻³	1x10 ⁻¹²	C(1x10 ⁻¹²)	CFE0H3
CAL0H3	T.S. constant for AL(OH) ₃	(mol.L ⁻¹) ²	1x10 ⁻¹⁵	C(1x10 ⁻¹⁵)	CAL0H3
f ₁	activity coefficient		0.84	T(0.67,0.84,1.01)	F1
f ₂	activity coefficient		0.499	T(0.399,0.499,0.599)	F2
f ₃	activity coefficient		0.201	T(0.18,0.201,0.22)	F3
KCAS04	gypsum solubility	(mol.L ⁻¹) ²	2.4x10 ⁻⁵	LN(2.4x10 ⁻⁵ , 1.05,2.14x10 ⁻⁵ , 2.75x10 ⁻⁵)	KCAS04
K ₁	dissociation constant for HCO ₃ ⁰	(mol.L ⁻¹)	5.012x10 ⁻⁷	C(5.01x10 ⁻⁷)	K1
K ₂	dissociation constant for HCO ₃ ⁻	(mol.L ⁻¹)	5.012x10 ⁻¹¹	C(5.012x10 ⁻¹¹)	K2
KCAC03	calcite solubility	(mol.L ⁻¹) ²	4.48x10 ⁻⁹	LN(4.48x10 ⁻⁹ , 1.05,3.89x10 ⁻⁹ , 5.13x10 ⁻⁹)	KCAC03
KFEO0H	FE00H solubility	(mol.L ⁻¹) ²	3.98x10 ¹	LN(3.98x10 ¹ , 3.16,1.27, 1.27x10 ³)	KFEO0H
CAL0H2	T.S. constant for AL(OH) ₂	(mol.L ⁻¹)	5.0x10 ⁻¹⁰	C(5.0x10 ⁻¹⁰)	CAL0H2
CAL0H	T.S. constant for AL0H	(mol.L ⁻¹)	1.07x10 ⁻⁵	C(1.07x10 ⁻⁵)	CAL0H
KBAS	log basaluminite solubility constant	(mol.L ⁻¹) ²	22.7	LN(22.7,1.02, 21.7,23.7)	KBAS
XKFe3	fraction of Fe ³⁺ from redox reactions	(unitless)	0.01	T(0.005,0.01,0.05)	XKFE3

Key to Probability Distributions:

C - Constant (single value)
 T - Triangular (min., mode, max.)
 U - Uniform (min., max.)
 LN - Lognormal (geo. mean, geo. std. dev., min., max.)
 N - Normal (mean, std.dev.,min.,max.)

Notes

T.S. = thermodynamic stability constants.
 C.B. = charge balance equation
 * = input parameters are required for each layer.

4.3 Rate of Pyrite Oxidation Calculated by a Deterministic Simulation

In this section model predictions of the variation in pyrite oxidation are presented as a function of month and depth.

4.3.1 Monthly Variations

In Figures 4.1 and 4.2, monthly variations in the rate of pyrite oxidation per unit volume of tailings are presented for depths of 0.2 m and 1.0 m, for two different pH conditions. In Case 210 the pH of the tailings porewater is buffered at about 3.5 by aluminum hydroxide and ferric hydroxide precipitates present in the tailings. In Case 410 only ferric hydroxide precipitate is present and the pH of the porewater is buffered at approximately 1.7.

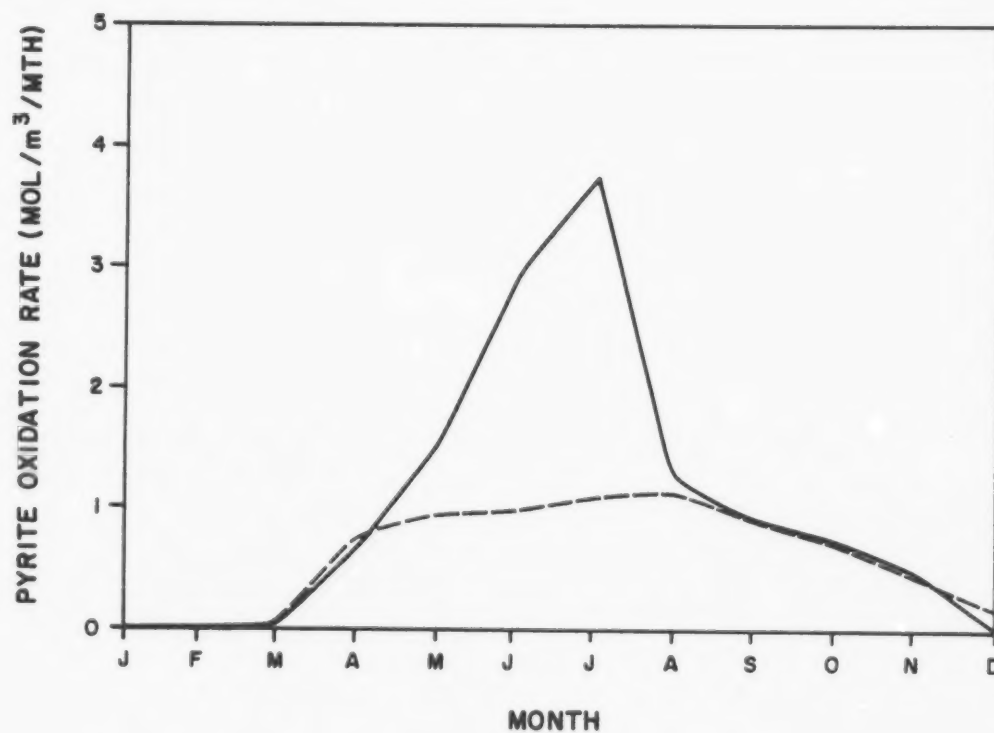
All four curves indicate that there is a strong temperature dependence with near zero oxidation rates during the winter months as expected. The model predicts that the rate of pyrite oxidation reaches a peak rate in July at the shallow depth, 0.2 m, and in August at the 1.0m depth. These are caused by a temperature peak in July at 0.2 m depth and in August at 1.0m depth (see Figures A.2 and A.4 in Appendix A for the annual variation in temperature).

The predictions given in Figures 4.1 and 4.2 also indicate that much higher oxidation rates occur during the warm weather months when the porewater pH is near 3.5 (Case 210) than when the pH is 1.7 (Case 410). This results from the rate of bacterial oxidation being a maximum near a pH of 3.25.

4.3.2 Depth Profile

Figure 4.3 presents a plot of the rate of pyrite oxidation as a function of depth for years one, four and ten during the month of June. During years one and ten the profiles for the rates of pyrite oxidation are very similar. It is during these periods that control is by chemical oxidation. In year one, calcite is present in all layers (Case 111) and the pH of the tailings porewater is buffered at about 6.4 to 6.6. In year ten only ferric hydroxide

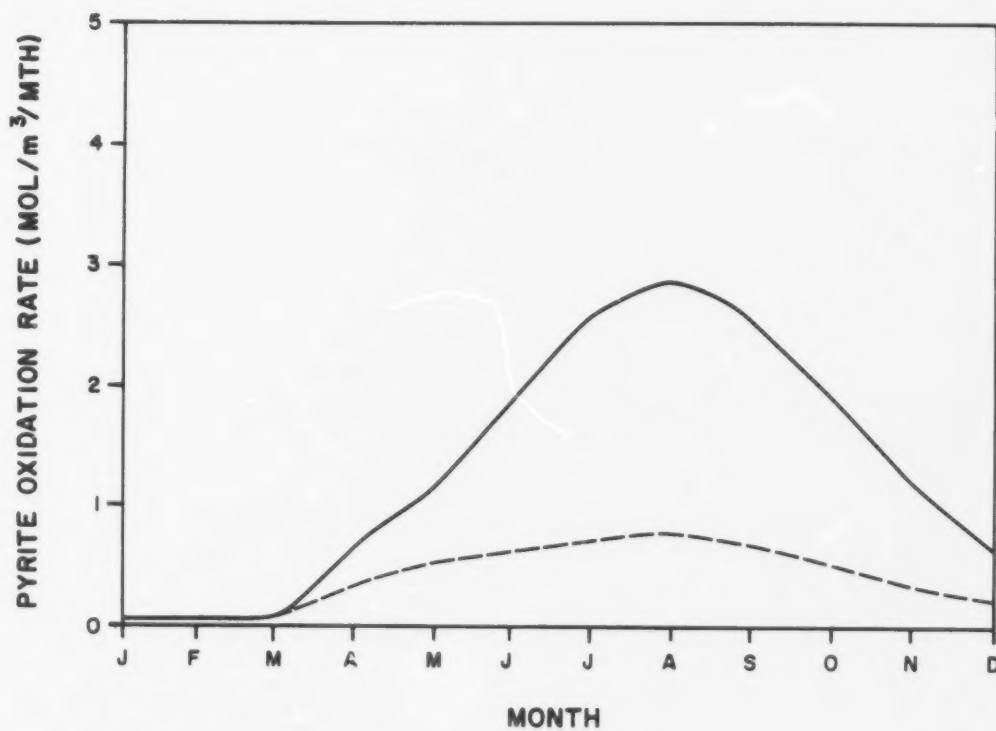
FIGURE 4.1
RATE OF PYRITE OXIDATION vs. MONTH
AT 0.2m DEPTH



LEGEND

- NO CALCITE / $\text{Fe}(\text{OH})_3$ AND $\text{Al}(\text{OH})_3$ PRESENT
 ---- NO CALCITE / $\text{Fe}(\text{OH})_3$ PRESENT / $\text{Al}(\text{OH})_3$ ABSENT

FIGURE 4.2
RATE OF PYRITE OXIDATION vs. MONTH
AT 1.0m DEPTH



LEGEND:

- NO CALCITE / $\text{Fe}(\text{OH})_3$ AND $\text{Al}(\text{OH})_3$ PRESENT
---- NO CALCITE / $\text{Fe}(\text{OH})_3$ PRESENT / $\text{Al}(\text{OH})_3$ ABSENT

is present in all the layers and the pH is buffered at about 1.7 (Case 410). The bacterial activity in both cases is low because of the unfavourable pH conditions. In contrast, during year four when the solid phase system buffers the pH at about 3.5, bacterial oxidation is the controlling factor. As suggested by the curves on Figure 4.3 the rate of pyrite oxidation per unit volume of tailings is about 6 times greater when bacteria-assisted oxidation controls than when chemical oxidation controls.

4.4 Acid Flux Calculated by a Deterministic Simulation

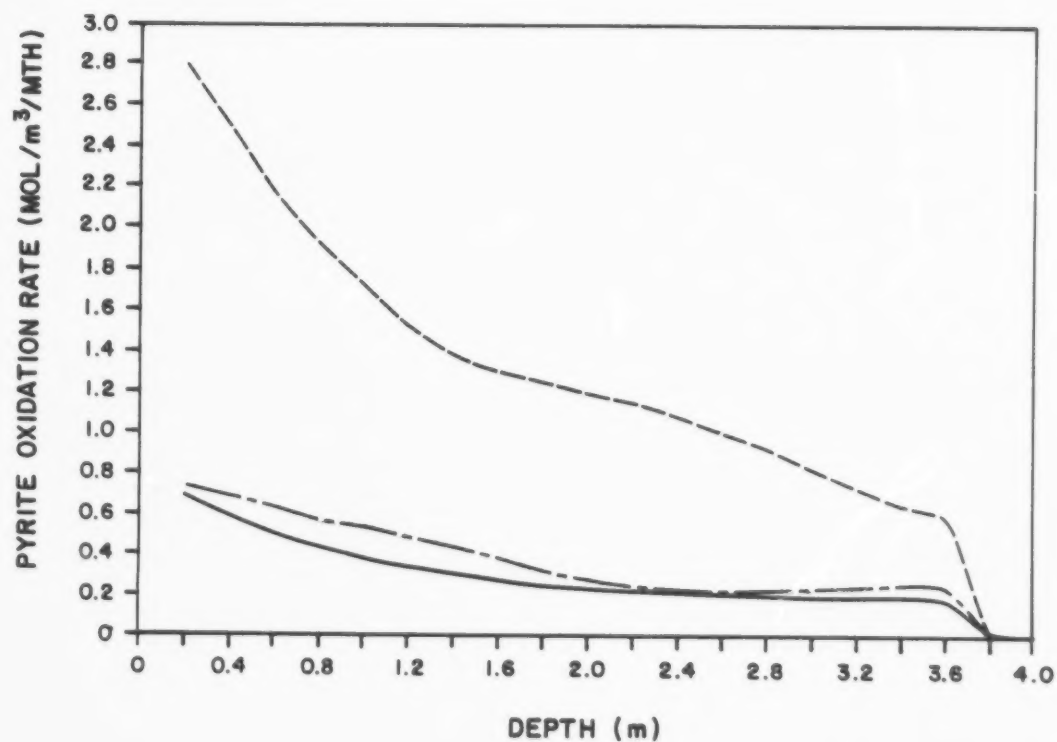
It should be noted that the optimal pH for bacterial mediated oxidation can shift to lower values with time in real systems. Evidence for adaptation to low pH is given by Bruynesteyn (1980). This feature, however, is not built into the model and the implications of this for the long term awaits further assessment.

4.4.1 Monthly Acid Flux

Monthly variations in the acid flux are displayed on Figures 4.4 and 4.5 for the same two cases (i.e. Cases 210 and 410) and for the two same depths (i.e. depths of 0.2 m and 1.0 m) as were described for the rate of pyrite oxidation in Section 4.3. The curves indicate that during the key acid-producing, warm weather, months there is a higher acid flux at a pH of 3.5 (Case 210) than at a pH of 1.7 (Case 410). This is expected since bacterial activity is near its maximum at a pH of 3.5.

The results also indicate that the time of year in which a layer experiences a maximum acid flux increase with depth; i.e. at 0.2 m the maximum acid flux is in July, month 7, whereas at 1.0 m the maximum flux is in October, month 10. The monthly acid flux is highly sensitive to the infiltration rate and to the rate of pyrite oxidation corresponding to the same time period and depths, Figure 4.1 and 4.2. The lag time with depth is attributable, in part, to the time required for infiltrating rainwater to move from layer to layer.

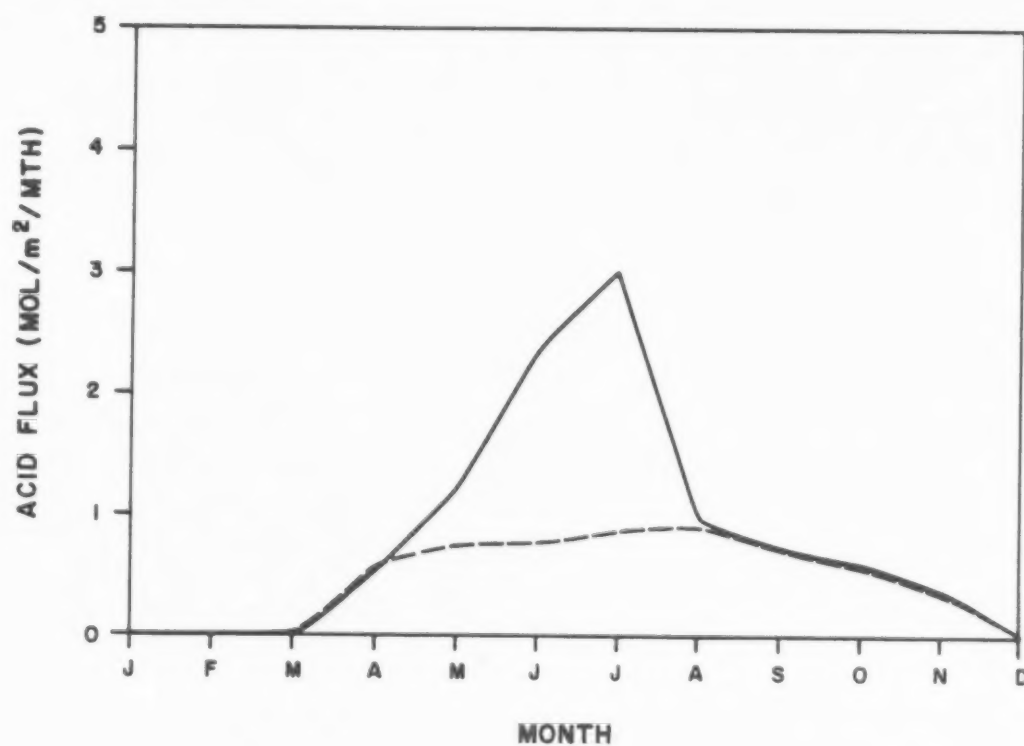
FIGURE 4.3
RATE OF PYRITE OXIDATION vs. DEPTH
FOR THE MONTH OF JUNE



LEGEND:

— YEAR 1
- - - YEAR 4
- · - YEAR 10

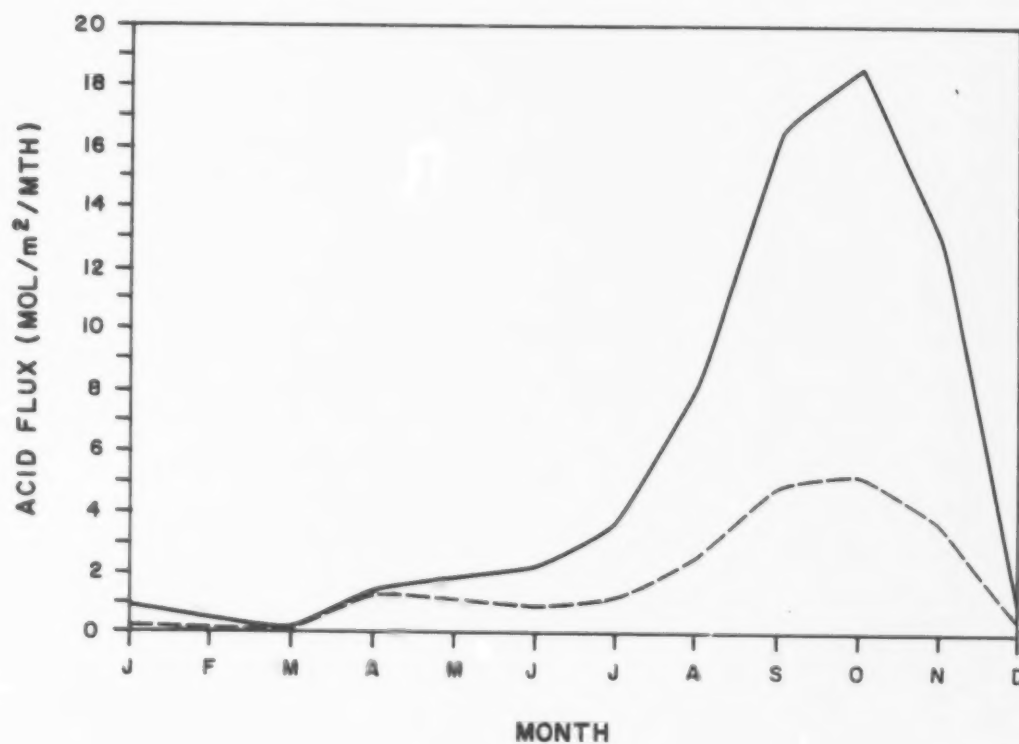
FIGURE 4.4
ACID FLUX
AS A FUNCTION OF MONTH
AT 0.2m DEPTH



LEGEND:

- NO CALCITE / $\text{Fe}(\text{OH})_3$ AND $\text{Al}(\text{OH})_3$ PRESENT
- - - NO CALCITE / $\text{Fe}(\text{OH})_3$ PRESENT / $\text{Al}(\text{OH})_3$ ABSENT

FIGURE 4.5
ACID FLUX
AS A FUNCTION OF MONTH
AT 1.0m DEPTH



LEGEND:

- NO CALCITE / Fe(OH)₃ AND Al(OH)₃ PRESENT
- - - NO CALCITE / Fe(OH)₃ PRESENT / Al(OH)₃ ABSENT

The differences in acid flux in the simulation are also a function of the pH. When the aluminum solid is present the pH is buffered at a value of about 3.5. This pH value is also close to the optimum pH for bacterial oxidation and hence higher rates and fluxes are expected. When only ferric hydroxide precipitate is present, the pH remains around 1.5 to 2.0 and the oxidation rates are lower.

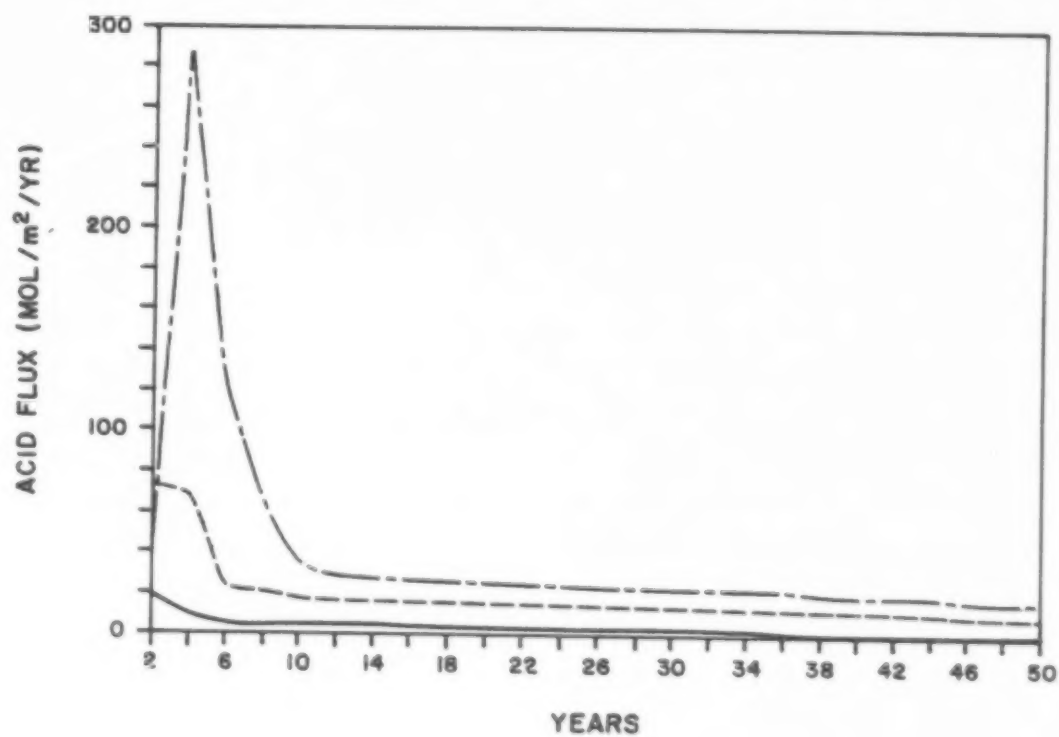
4.4.2 Annual Acid Flux

Figure 4.6 presents a plot of the annual acid flux at three depths over a time period of 50 years. At the end of the first ten year period, the acid flux reaches a quasi steady state rate at all three depths. The periods of maximum acid generation coincide with conditions of optimal bacterial activity, i.e. when the pH of the tailings porewater is buffered at approximately 3 to 3.5 by basaluminite present in the tailings solids. Once all the basaluminite is dissolved and the pH declines to 1.5 to 2.0, the rate of pyrite oxidation decreases from that of the optimal bacterial growth conditions.

4.4.3 Cumulative Acid Flux

The cumulative acid flux, which equals the total acid generated from time =0 to time =t for a given depth of tailings, is shown in Figure 4.7 for tailings depths of 0.2, 1.0 and 2.2 m. At the end of the 50 year simulation period the cumulative acid fluxes from the three layers are approximately proportional to the ratio of the depths of the layers (e.g. the acid flux from layer 5 located at a depth of 1.0m is approximately 5 times the acid flux from layer 1 located at a depth of 0.2m). Since the pyrite content is assumed to be initially uniform with depth, the acid flux in Figure 4.7 suggest that an equal amount of pyrite has been oxidized at each depth of the unsaturated zone over the 50 year time frame. This suggests that the average oxidation rate over all depths is equivalent to a zero order with respect to oxygen, yielding a half order dependency with respect to flux. This constant rate would continue until pyrite is depleted in the surficial zone. The calculated fluxes

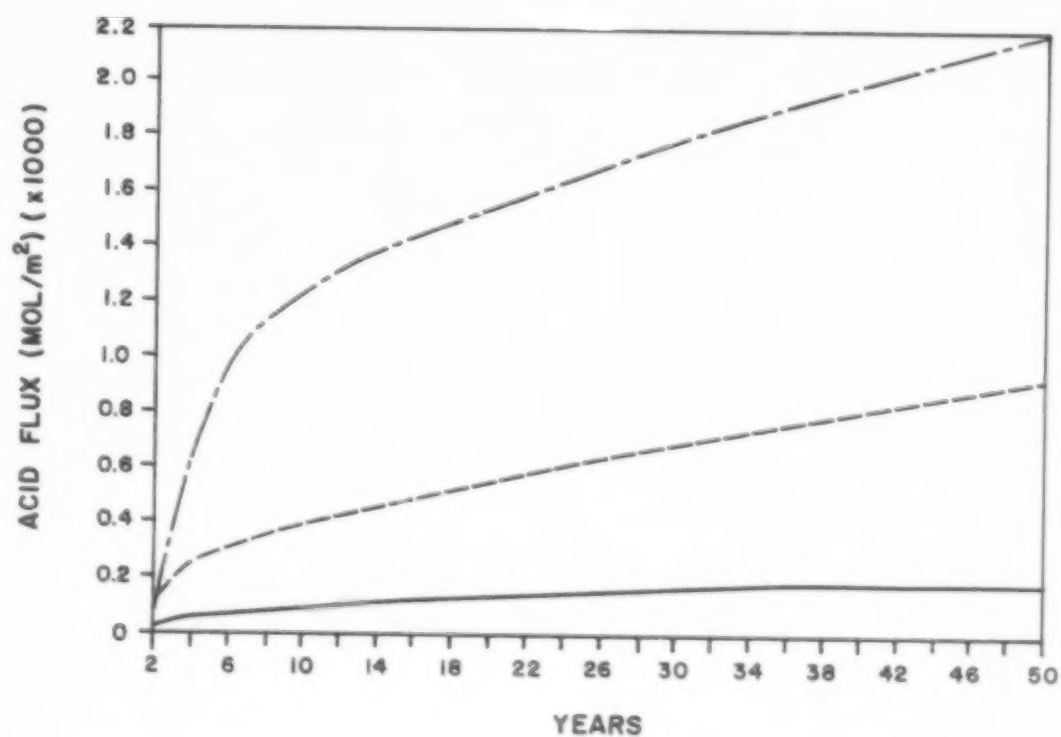
FIGURE 4.6
SIMULATION OF YEARLY ACID FLUX
FOR LAYERS I, 5 AND II



LEGEND :

- 0.2m DEPTH
- - - 1.0m DEPTH
- . - 2.2m DEPTH

FIGURE 4.7
SIMULATION OF CUMULATIVE ACID FLUX
FOR LAYERS I, 5 AND II



LEGEND :

- 0.2m DEPTH
- .-.- 1.0m DEPTH
- .-.- 2.2m DEPTH

indicate the approximately 40% of the pyrite has been oxidized over this 50 year time frame.

4.4.4 Probabilistic Assessment

In order to assess the upper and lower limits of the acid flux, a probabilistic simulation comprising 100 trials was performed using the RATAP code. The simulation was conducted for a 20 year time period which captures the period of maximum activity, for tailings characterized by the input parameter values given on table 4.1.

Figures 4.8 and 4.9 present frequency histograms of the monthly acid flux from layer five, 1.0 m below the tailings surface during the month of June in years 5 and 16, respectively. The frequency histograms presented on the figures were fitted with several probability distributions using commercially available statistical software. A lognormal distribution best described the frequency histogram shown in Figure 4.8. In contrast, a normal distribution was found to describe the histogram plotted in Figure 4.9. The difference in the monthly acid flux's distribution is attributable to the changing sensitivity of the model calculations to the various input parameters and hence their distributions. The model's calculations appear to fit a lognormal distribution during the period of large acid production and a normal distribution during the period of low acid production.

Acid fluxes predicted for the month of June at depths 1.0 m and 2.2 m below the tailings surface are presented in Figures 4.10 and 4.11, respectively. The flux curves shown on these figures are plots of the geometric mean values and the predicted upper and lower limits (i.e. maximum and minimum values) from 100 trials. During year one, the monthly acid flux had a mean value of $6 \text{ mol.m}^{-2}.\text{mth}^{-1}$, at a depth of 2.2m and minimum and maximum values (lower and upper limits) of 0.5 and $80 \text{ mol.m}^{-2}.\text{mth}^{-1}$, respectively. By year 16, the mean value in June at the 2.2 m depth had declined to approximately $5 \text{ mol.m}^{-2}.\text{mth}^{-1}$ while the lower and upper limits ranged from 0 to $21 \text{ mol.m}^{-2}.\text{mth}^{-1}$. In contrast, the mean, minimum and maximum acid flux values calculated for the

FIGURE 4.8
FREQUENCY HISTOGRAM
FOR THE MONTHLY ACID FLUX IN LAYER 5
DURING JUNE, YEAR 5
(1.0m BELOW THE TAILINGS SURFACE)

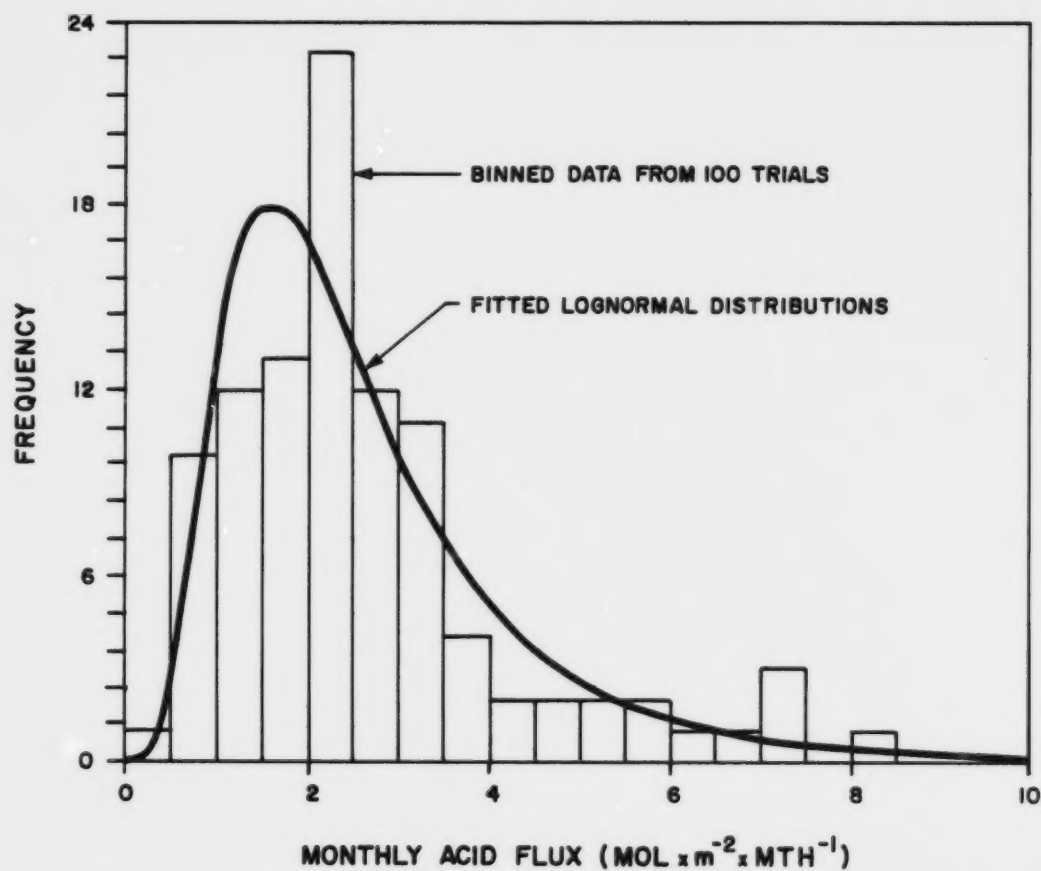


FIGURE 4.9
FREQUENCY HISTOGRAM
FOR THE MONTHLY ACID FLUX IN LAYER 5
DURING JUNE, YEAR 16
(1.0m BELOW THE TAILINGS SURFACE)

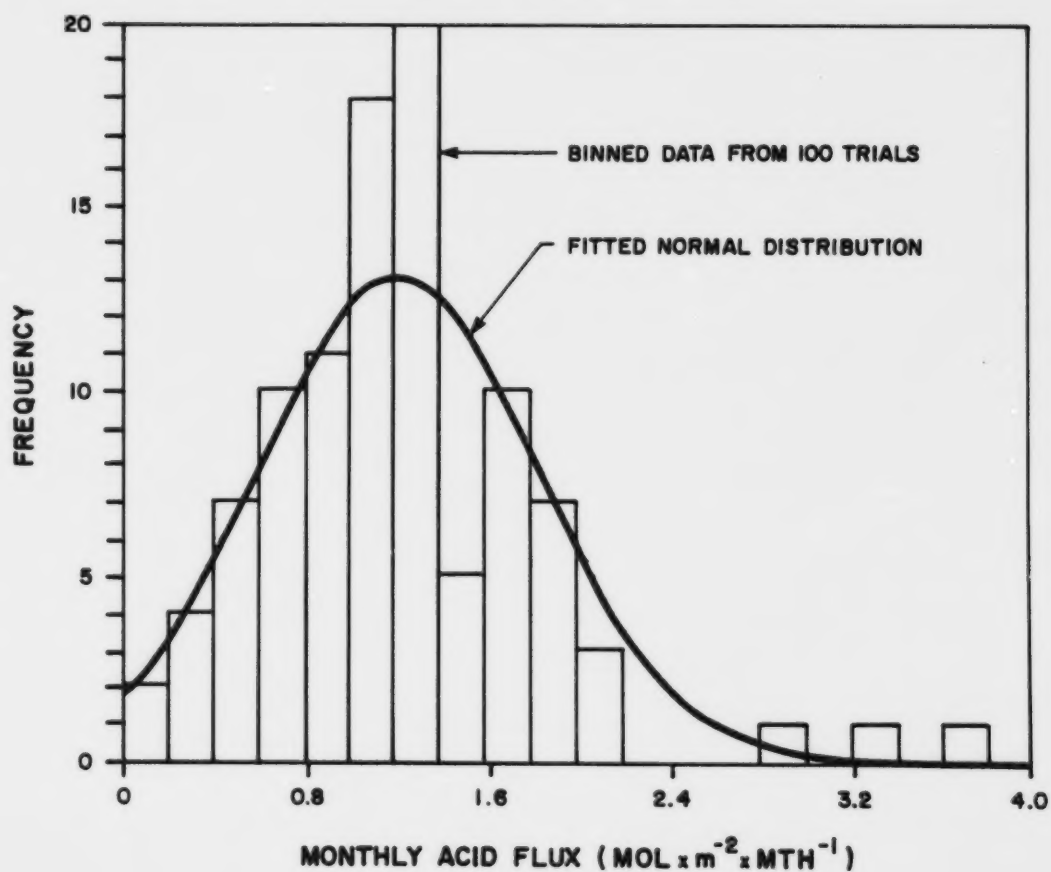
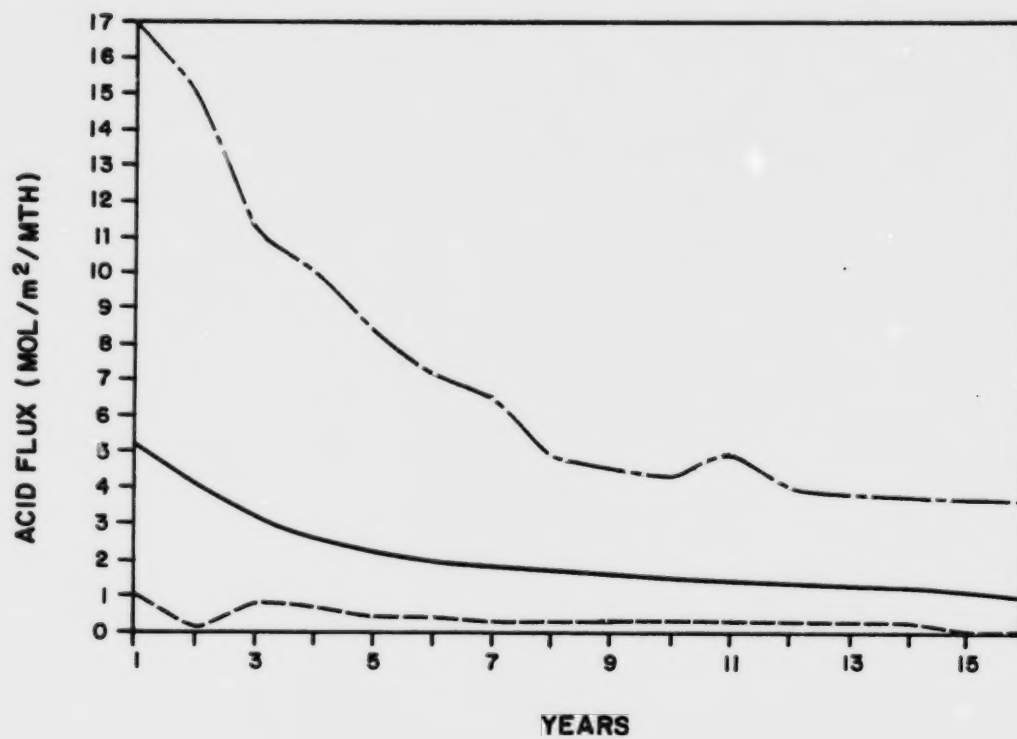


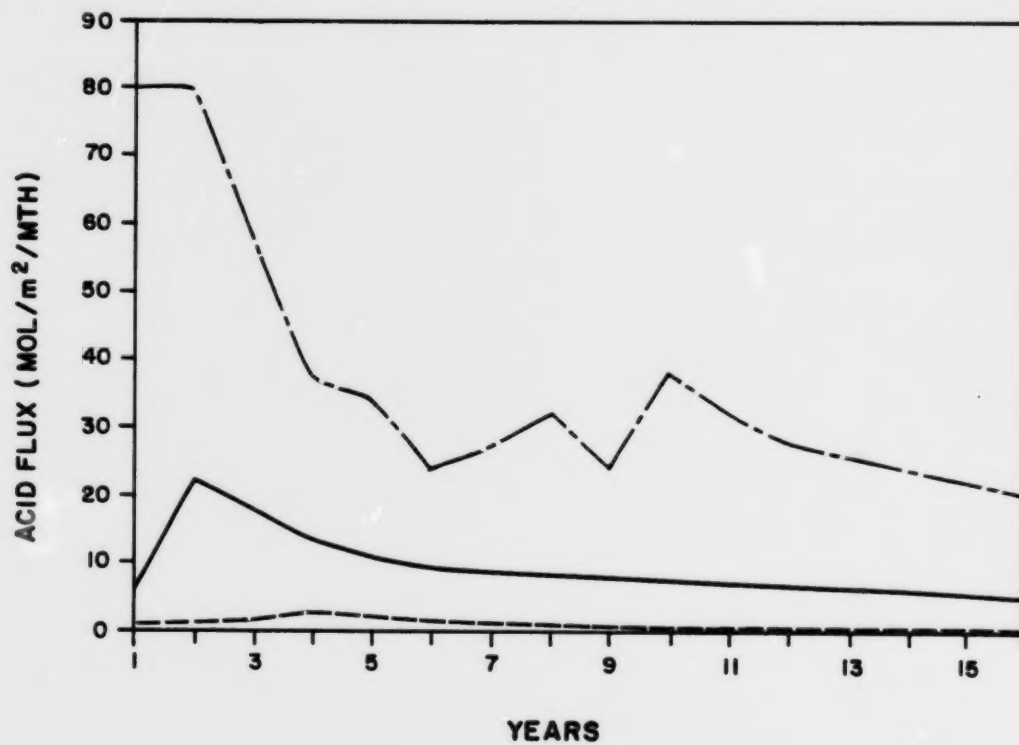
FIGURE 4.10
ACID FLUX
FOR THE MONTH OF JUNE vs. YEAR
AT 1.0m DEPTH



LEGEND:

- GEOMETRIC MEAN
- - - UPPER LIMIT
- . - LOWER LIMIT

FIGURE 4.11
ACID FLUX
FOR THE MONTH OF JUNE vs. YEAR
AT 2.2m DEPTH



LEGEND:

- GEOMETRIC MEAN
- - - UPPER LIMIT
- . - LOWER LIMIT

shallower depth of 1.0 m (see Figure 4.10) were much lower. This difference is mainly due to the depth of oxygen penetration.

The yearly acid fluxes transported through interfaces located 1.0m and 2.2 m below the tailings surface are presented in Figures 4.12 and 4.13. At the 1.0 m depth, the acid flux peaked in year one. The geometric mean values from 100 trials equalled $125 \text{ mol.m}^{-2}.\text{yr}^{-1}$ and the minimum and maximum predicted values were 25 and $375 \text{ mol.m}^{-2}.\text{yr}^{-1}$. At a depth of 2.2 m the yearly acid flux peaked in year two. The geometric mean value from 100 trials was $250 \text{ mol.m}^{-2}.\text{yr}^{-1}$; the lower and upper limits were 30 and $870 \text{ mol.m}^{-2}.\text{yr}^{-1}$ respectively.

In both figures, the calculated acid fluxes decrease with time. The mean acid flux in year 16 at a depth of 1.0 m is $25 \text{ mol.m}^{-2}.\text{yr}^{-1}$ while at a depth of 2.2 m, it is $80 \text{ mol.m}^{-2}.\text{yr}^{-1}$. The lower and upper limits on the curves are also at their minimum values in year 16 equalling 0 and $60 \text{ mol.m}^{-2}.\text{yr}^{-1}$, respectively at the 1.0 m depth and 10 and $300 \text{ mol.m}^{-2}.\text{yr}^{-1}$, respectively at the 2.2 m depth.

The mean acid flux in year 16 at a depth of 2.2m, $80 \text{ mol.m}^{-2}.\text{yr}^{-1}$, compares favourably with measured acid fluxes of non-operating Elliot Lake properties.

4.5 Sensitivity/Uncertainty Analysis

In probabilistic modelling, the terms sensitivity and uncertainty analysis refer to techniques which seek to define the relationship(s) between model inputs and model predictions. The term "sensitivity analysis" refers to establishing the sensitivity of the magnitude of the model output to changes in the magnitudes of the input parameters. The term "uncertainty analysis" refers to establishing how much the uncertainty (or spread) associated with each parameter contributes to the total uncertainty (or spread) of the model predictions. The sensitivity and uncertainty analysis techniques are useful methods for isolating and/or ranking the most "important" parameters, i.e. those which have the greatest influence on the model predictions. The techniques are equally useful in identifying those parameters and pathways

which are important and also those which are unimportant and thus can be de-emphasized in planning future research investigations.

The sensitivity/uncertainty analysis technique employed in this study is the sensitivity index. The sensitivity index for a particular input parameter is calculated by holding all other parameters constant at their nominal values and calculating the desired output at the minimum and maximum values of the input parameter being studied.

The sensitivity index (SI) is calculated as:

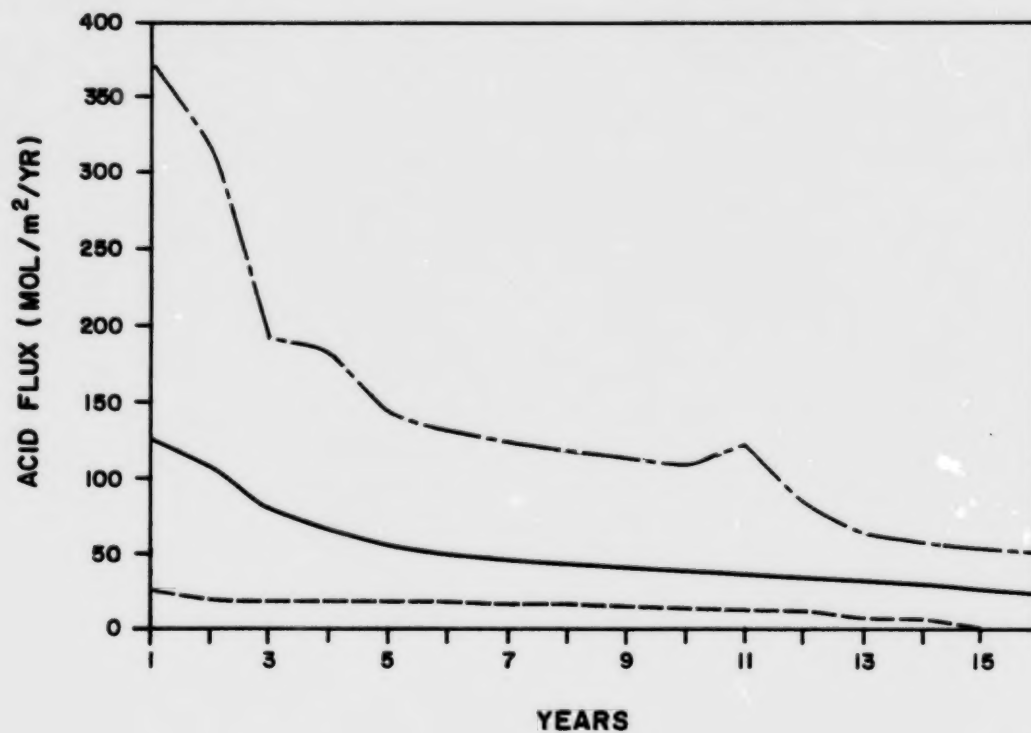
$$SI = 1 - \frac{\text{Low Result}}{\text{High Result}}$$

Parameters with SI values near 1 are considered to be important, whereas parameters with SI values near 0 have little influence on the model calculations. This method does not account for interaction between parameters that may be important but, has been shown to be a fairly robust technique in other work (SENES, 1985).

Tables 4.2. to 4.5. present the input parameters which have the greatest influence on the rate of pyrite oxidation and the monthly acid flux at various time periods and depths. In order to facilitate a reasonable computer run time, the soil parameters randomly sampled for layer 1 were used for the remaining layers. In other words, the tailings were treated as having uniform characteristics during each trial but the characteristics were allowed to vary randomly from trial to trial. This constraint did not detract from the sensitivity analysis, rather it reduced the run time and simplified the data analysis.

The time periods analyzed were for the months of January and June during years two and ten; i.e. months 13, 18, 121 and 126. Three depths were studied, two in the unsaturated zone at 0.2 m and 1.0 m below the tailings surface, and the other at the top layer of the saturated zone, 2.2 m below the tailings

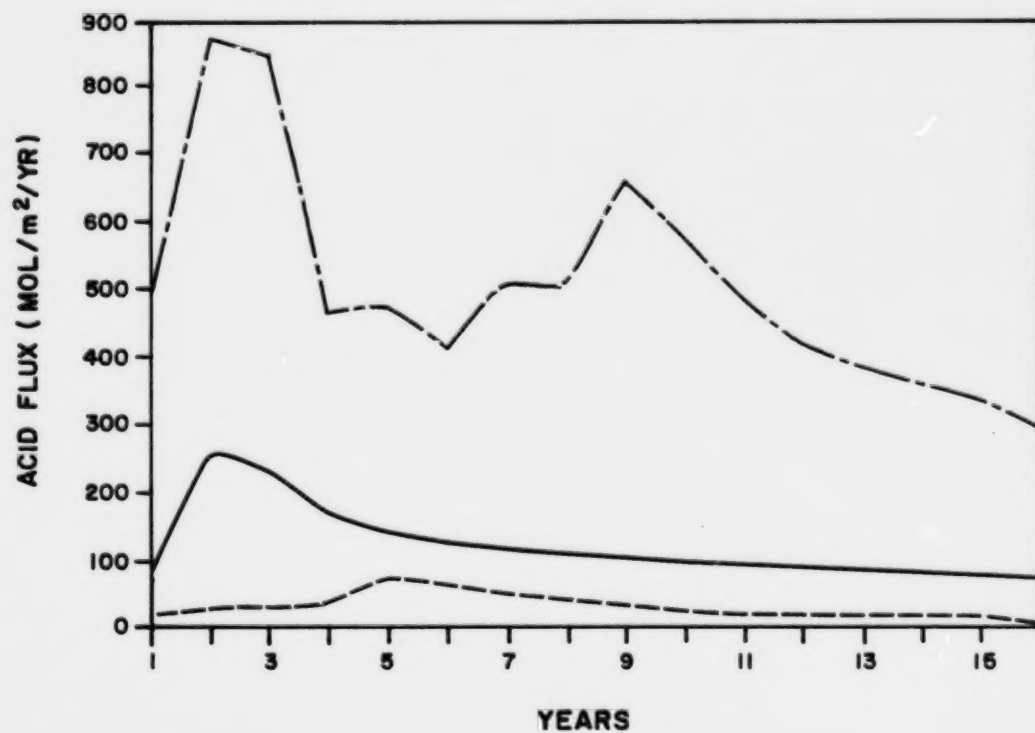
FIGURE 4.12
YEARLY ACID FLUX vs. TIME
AT 1.0m DEPTH



LEGEND:

- GEOMETRIC MEAN
- UPPER LIMIT
- .-.- LOWER LIMIT

FIGURE 4.13
YEARLY ACID FLUX vs. TIME
AT 2.2 m DEPTH



LEGEND:

- GEOMETRIC MEAN
- UPPER LIMIT
- .- LOWER LIMIT

Table 4.2

**INFLUENCE OF INPUTS ON ACID FLUX
AND RATE OF PYRITE OXIDATION
(JANUARY, YEAR TWO)**

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux (mol.m ⁻² .mth ⁻¹)			Rate of Pyrite Oxidation (mol.m ⁻³ .mth ⁻¹)	
	0.2m	1.0m	2.2m	0.2m	1.0m
SI ≥ 0.70	XCAC03 (0.916)	KCONST (0.947)	KCONST (0.951)	KCONST (0.989)	KCONST (0.956)
	XP (0.790)	V1 (0.783)	V1 (0.900)	XCAC03 (0.721)	XCAC03 (0.878)
	KCONST (0.719)	XCAC03 (0.748)	XCAC03 (0.847)		
0.70 > SI ≥ 0.4	V1 (0.675)	V12 (0.613)	HE (0.648)		HE (0.445)
	SATCT (0.647)	V9 (0.432)	V7 (0.481)		
	XPYR (0.636)		V12 (0.450)		
			V3 (0.447)		
0.4 > SI ≥ 0.1		V10 (0.291)	V8 (0.353)	XP (0.352)	XPYR (0.318)
		HE (0.278)	V6 (0.341)	XPYR (0.212)	V1 (0.105)
		V11 (0.233)	XPYR (0.305)		
			V9 (0.236)		
			XP (0.215)		
			V10 (0.203)		
			V11 (0.201)		
			V5 (0.137)		

Table 4.3

**INFLUENCE OF INPUTS ON ACID FLUX
AND RATE OF PYRITE OXIDATION
(JUNE, YEAR TWO)**

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux (mol.m ⁻² .mth ⁻¹)			Rate of Pyrite Oxidation (mol.m ⁻³ .mth ⁻¹)	
	0.2m	1.0m	2.2m	0.2m	1.0m
SI ≥ 0.70	KCONST (0.917)	KCONST (0.942)	KCONST (0.975)	KCONST (0.979)	KCONST (0.982)
	XP (0.903)	V6 (0.784)	V6 (0.900)	XPYR (0.927)	XCAC03 (0.881)
	XPYR (0.864)		XCAC03 (0.885)	XP (0.903)	
	XCAC03 (0.755)			XCAC03 (0.858)	
0.70 > SI ≥ 0.4	NR (0.433)	V3 (0.597)	HE (0.515)	NR (0.433)	HE (0.265)
		XCAC03 (0.592)	V12 (0.464)		
		XP (0.567)	V8 (0.458)		
		V2 (0.465)	V1 (0.413)		
			V3 (0.411)		
0.4 > SI ≥ 0.1	EA1 (0.289)	XPYR (0.363)	V2 (0.396)	EA1 (0.289)	XPYR (0.265)
	HE (0.224)	HE (0.328)	XPYR (0.305)	HE (0.224)	XP (0.165)
	UMAX (0.165)	V5 (0.244)	V9 (0.261)	UMAX (0.164)	
	V6 (0.137)	SATCT (0.147)	XP (0.240)	V6 (0.135)	
	NT (0.123)	V4 (0.132)	V10 (0.177)	NT (0.123)	
			V11 (0.143)		

Table 4.4

**INFLUENCE OF INPUTS ON ACID FLUX
AND RATE OF PYRITE OXIDATION
(JANUARY, YEAR TEN)**

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux (mol.m ⁻² .mth ⁻¹)			Rate of Pyrite Oxidation (mol.m ⁻³ .mth ⁻¹)	
	0.2m	1.0m	2.2m	0.2m	1.0m
SI ≥ 0.70	XP (0.979)	V1 (0.878)	HE (0.844)	XP (1.00)	HE (1.00)
		XP (0.760)	V1 (0.806)	KCONST (1.00)	KCONST (0.996)
0.70 > SI ≥ 0.4	HE (0.599)	V12 (0.677)	V12 (0.651)	HE (0.533)	XP (0.523)
	XCAC03 (0.426)	HE (0.593)	V7 (0.629)		
	XPYR (0.404)	EA1 (0.578)	V8 (0.594)		
		KBAS (0.486)	XCAC03 (0.551)		
		KFE00H (0.476)	NT (0.518)		
		KCONST (0.461)	F1 (0.515)		
			KCONST (0.512)		
			V3 (0.508)		
			V2 (0.496)		
			SATCT (0.488)		
			V4 (0.470)		
			XALOH3 (0.456)		

Table 4.4 continued

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux (mol.m ⁻² .mth ⁻¹)			Rate of Pyrite Oxidation (mol.m ⁻³ .mth ⁻¹)	
	0.2m	1.0m	2.2m	0.2m	1.0m
0.4 > SI ≥ 0.1	V1 (0.343)	NR (0.326)	XP (0.388)	XCAC03 (0.378)	XCAC03 (0.348)
	NR (0.233)	V9 (0.325)	NR (0.334)	XPYR (0.342)	XPYR (0.317)
	EA1 (0.210)	V10 (0.292)	XPYR (0.330)	NR (0.191)	EA1 (0.245)
	KCONST (0.197)	XPYR (0.268)	V6 (0.236)	EA1 (0.173)	KFE00H (0.243)
	KFE00H (0.173)	V11 (0.265)	EA1 (0.234)	KFE00H (0.142)	NR (0.192)
			V9 (0.214)		V1 (0.133)
			V10 (0.179)		KBAS (0.129)
			V11 (0.177)		
			UMAX (0.123)		

Table 4.5

INFLUENCE OF INPUTS ON ACID FLUX
AND RATE OF PYRITE OXIDATION
(JUNE, YEAR TEN)

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux (mol.m ⁻² .mth ⁻¹)			Rate of Pyrite Oxidation (mol.m ⁻³ .mth ⁻¹)	
	0.2m	1.0m	2.2m	0.2m	1.0m
SI ≥ 0.70	XP (0.999)	HE (0.982)	V6 (0.900)	XP (1.0)	HE (1.0)
	KCONST (0.999)	XP (0.797)	HE (0.723)	KCONST (1.0)	XP (0.821)
0.70 > SI ≥ 0.4	KFE00H (0.442)	V6 (0.657)	EA1 (0.621)	V6 (0.443)	KFE00H (0.651)
	V6 (0.438)	KFE00H (0.544)	XP (0.604)	KFE00H (0.440)	KBAS (0.562)
		EA1 (0.509)	KFE00H (0.594)		EA1 (0.489)
		KBAS (0.450)	KCONST (0.473)		
		V5 (0.421)	KBAS (0.465)		
			V12 (0.442)		
			V3 (0.424)		
			V1 (0.421)		
0.4 > SI ≥ 0.1	NR (0.334)	NR (0.355)	V2 (0.373)	NR (0.332)	KCONST (0.358)
	XPYR (0.263)	XPYR (0.314)	NR (0.367)	XPYR (0.260)	NR (0.333)
	XCAC03 (0.188)	V4 (0.291)	XPYR (0.321)	XCAC03 (0.186)	V6 (0.303)
	EA1 (0.180)	V3 (0.232)	V8 (0.297)	EA1 (0.178)	XPYR (0.251)
	HE (0.134)	V2 (0.144)	V9 (0.185)	HE (0.133)	UMAX (0.149)
		UMAX (0.118)	V10 (0.154)		V5 (0.133)

Table 4.5 continued.

SI Range	Parameter (Sensitivity Index)				
	Monthly Acid Flux ($\text{mol.m}^{-2}.\text{mth}^{-1}$)			Rate of Pyrite Oxidation ($\text{mol.m}^{-3}.\text{mth}^{-1}$)	
	<u>0.2m</u>	<u>1.0m</u>	<u>2.2m</u>	<u>0.2m</u>	<u>1.0m</u>
		KCONST (0.118)	V11 (0.128)		XALOH3 (0.109)
			UMAX (0.118)		
			XCAC03 (0.110)		

surfaces.

The sensitivity index was calculated for both monthly acid flux and the rate of pyrite oxidation at the specified depths. Pyrite oxidation was not significant at the 2.2m depth and therefore values are not provided.

The results of the sensitivity analysis permit several conclusions to be made about the influence of the input parameters on the model predictions. The influence of the most important parameters on the rate of pyrite oxidation and on the quantity of acid generated are discussed below under the respective headings.

Rate of Pyrite Oxidation

1. At all time periods and depths, the rate of pyrite oxidation is very sensitive to changes in the chemical rate constant, KCONST, and to a lesser extent changes in the mass fraction of pyrite, XPYR.
2. Variation in the mass fraction of calcite, XCACO3, greatly affects the rate of pyrite oxidation in year two but has a lesser influence in year ten. This results from the calcite being mainly leached from the tailings within the first ten years.
3. The rate of pyrite oxidation at the shallow depth, layer 1 (0.2 m), and the deeper depth, layer 5 (1.0 m), is quite sensitive to change in the microbial population density, XP, at all time periods.
4. The air entry value, HE, is very important in determining the rate of pyrite oxidation in layer 5 (1.0 m) whereas in layer 1 (0.2 m) it is of lesser importance. In addition the relative importance of HE in layer 5 appears to increase from year 2 to year 10. The air entry value is important because it influences the gaseous diffusion coefficient of oxygen.

Monthly Acid Flux

1. At year two the monthly acid flux for all layers is very sensitive to changes in the chemical rate constant, KCONST, and the initial mass fraction of calcite, XCACO3. At year ten, the monthly acid flux is less sensitive to variations in these inputs.
2. The monthly acid flux in the unsaturated zone, layer 1 (0.2 m) and layer 5 (1.0 m), is sensitive at most time periods to the microbial population density, XP, and the mass fraction of pyrite, XPYR.
3. The monthly acid flux is very sensitive, at all time periods, to the corresponding monthly infiltration rate, V1 to V12. Also, the deeper the layer in question, the greater the number of monthly infiltration rates that influence the acid flux.
4. The air entry value, HE, representing the grain size of the tailings and used to calculate the effective oxygen diffusivity, has an influence on the monthly acid flux, especially in the tenth year.

4.6 Priorities for Future Research

4.6.1 Introduction

The purpose of this section is to identify those parameters which should be given priority in future research. The objective of such research, would be to reduce the uncertainties associated with the input parameters such that the uncertainty (width of the distribution) associated with model calculations is reduced.

The results of the sensitivity/uncertainty analysis indicates that at least twenty three parameters play a significant role in the determination of the pyrite oxidation rate and/or the acid flux. They are: energy of activation (EA1), maximum specific growth rate (UMAX), bacterial population density (XP),

mass fractions of calcite (XCAC03), aluminum hydroxide (XALOH3) and pyrite (XPYR), chemical rate constant (KCONST), solubility constants for basaluminite (KBAS), and iron hydroxide (KFE00H), air entry value (HE), residual water content (NR), porosity (NT) and the twelve monthly infiltration rates (V1 to V12).

The parameters can be divided into two groups; site specific and nonsite specific. This distinction in the parameters is important because different types of data are required to reduce the associated uncertainties. For the site specific parameters, more detailed field sampling is required, whereas for the non-site specific parameters a more thorough literature search and/or detailed laboratory studies are appropriate.

It should also be noted that some parameters which one might expect to see on the list, are not present because they are calculated from other fundamental parameters in the model. For example, the effective diffusion coefficient for oxygen (DE) is determined from values of HE and NR which provide values for the air filled porosity (NA). Based upon the causal relationships between the basic and intermediate parameters, inferences can be drawn to explain the model sensitivity in terms of transport processes and bio-chemical processes (such as diffusion in terms of HE and NR).

4.6.2 Site Specific Parameters

The site specific parameters include the mass fractions of pyrite, calcite and aluminum hydroxide, the bacterial population density, the air entry value, residual water content, porosity, and infiltration rates.

Mass Fraction of Pyrite

The composition of pyrite in tailings, XPYR, varies from site to site. For typical pyritic uranium tailings, a 6% pyrite content has been reported (Beak, 1985). This nominal value was employed in the model runs and assumed to vary uniformly by $\pm 20\%$ about the nominal value. The available pyrite

surface area for oxidation is a function of the pyrite content and the pyrite grain size distribution. The rate of oxidation in turn is proportional to pyrite surface area. Hence the pyrite mass fraction influences oxidation kinetics and the flux of acidity.

Mass Fraction of Calcite

The mass fraction of calcite in the tailings is a function of several factors; whether or not limestone is found in the original ore and incompletely leached or is added in the mill, the purity of the limestone, and the amount of excess limestone added. The nominal value employed in the model run was 0.05% calcite and was assumed to vary uniformly by $\pm 100\%$ about the nominal value. The calcite mass fraction affects the pH of the porewater and the time required for the tailings to become acidic.

The pH directly affects the rate of pyrite oxidation and determines whether bacterial or chemical kinetics will dominate in the generation of acid. Hence calcite mass fraction relates to oxidation kinetics.

Mass Fraction of Aluminum Hydroxide

The composition of basaluminite, the aluminum hydroxide solid considered for tailings, varies from site to site. The nominal value employed in the model runs was 0.23% aluminum hydroxide with an assumed variability of $\pm 40\%$. This mean value was based upon the amount of aluminum leached in the leaching pachucas of Rio Algom. As with the two previous parameters it was assumed to be uniformly distributed.

The aluminum hydroxide mass fraction affects the pH of the porewater under conditions in which calcite has been depleted and hence influences the oxidation kinetics.



Bacterial Population Density

The bacterial population density, XP , on pyritic surfaces influence the rate of pyrite oxidation. It's effect upon model calculations occurs mainly in the surface layers (e.g. 0-0.2m).

In this study the bacterial population density was calculated to be 7.8×10^{-4} to $2.36 \times 10^{-2} \text{ g.m}^{-2}$. These values correspond to reported surface coverings of 1% (Chang and Myerson, 1983) and 30% (Le Roux et al., 1973). The variable was assumed to be lognormally distributed with a mean of $1.6 \times 10^{-3} \text{ g.m}^{-2}$ and a geometric standard deviation of 1.7.

Air Entry Values

The air entry value represents the height of the capillary fringe in the unsaturated zone and is influenced by the tailings grain size. A triangular probability distribution was assumed in this study with a minimum of -1.5m, a mode of -0.5m and a maximum of -0.05m. This parameter in conjunction with the residual water content controls the resident moisture content that in turn controls the oxygen diffusivity through the unsaturated zone. For this reason, a correlation between HE and NR may be quite high and warrants further study.

The importance of HE and NR increases (for monthly acid flux) from year two to year ten. This shift in importance was suggested by modelling results reported in Beak (1985). Those findings suggested that kinetic factors are more important at early times where-as oxygen transport (diffusion) will be more important as time progresses. The trend in the sensitivity analyses results reported here support those conclusions. The shift noted here is not as dramatic as that noted in Beak (1985) mainly because the range in DE values sampled in this study was only one order of magnitude compared to two orders of magnitude in the Beak Study.

Residual Water Content

The residual water content, NR, represents the value below which water will not percolate through the soil, but is held to the soil by surface tension. This term indirectly controls oxygen diffusivity and hence plays a role in oxygen transport.

A normal probabilistic distribution was assumed for the residual water content. Based on literature values for residual water content in tailings a mean value of $0.08 \text{ m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tail}}$ and a standard deviation of 0.01 was selected. Both the residual water content and air entry value were used to estimate the resident moisture content at any position in the tailings above the water table. There are in fact more sophisticated means of estimating moisture content in space and time. At present, however, these are awkward to use in such a model. What is needed here is a more precise means of estimating moisture content rather than more investigation into values of NR and HE.

Porosity

The porosity of a porous medium is the ratio of void volume to total unit volume. In this study the porosity of tailings is assumed to have a triangular probability distribution with a minimum of $0.45 \text{ m}^3 \cdot \text{m}^{-3}$, mode of $0.50 \text{ m}^3 \cdot \text{m}^{-3}$ and a maximum of $0.55 \text{ m}^3 \cdot \text{m}^{-3}$. Variations in the porosity affect oxygen transport by influencing the volume of oxygen which can infiltrate per unit mass of pyrite.

Monthly Infiltration Rates

Variations in the monthly infiltration rates, V1 to V12, especially the infiltration rate for the month of interest, have a large effect on the calculated acid flux. The effect of infiltration rate is related to dilution and its influence upon porewater, pH and therefore oxidation kinetics.



The infiltration rates employed are hypothetical data and were used to demonstrate the model. Because of the acid flux's high degree of sensitivity to this parameter, representative site specific data is considered to be a high priority input for a simulation of a specific site. The site specific data needed includes mean monthly values of precipitation runoff and evapotranspiration.

4.6.3 The Non-site Specific Parameters

The non-site specific parameters include the biological energy of activation, maximum specific growth rate, the solubility constants for basaluminite and iron hydroxide, and the chemical rate constant.

Biological Energy of Activation

The biological energy of activation, E_{A1} , is a measure of the amount of energy required for a biological process to occur. Literature values range from 11.7 (Lundgren and Silver, 1980) to $25.6 \text{ kcal.mol}^{-1}$ (Halbert et al., 1983).

The nominal value of $11.7 \text{ kcal.mol}^{-1}$ was selected for use in the model simulations because its use in the rate of biological pyrite oxidation (equation (B.2.5), Appendix B), produced results similar to experimental results of several other investigators (Malouf and Prater, 1961; Silverman and Lundgren, 1958; Belly and Brock, 1974). The activation energy directly affects oxidation kinetics.

Maximum Specific Growth Rate

The maximum specific growth rate, U_{MAX} , is the specific growth rate of the microbes under optimal conditions. It directly influences oxidation kinetics. Estimation of the value of U_{MAX} was made using experimental data reported for the specific growth rate of *T. Ferroxidans* grown on pyritic materials at known temperature and pH conditions. The estimated U_{MAX} values ranged from 11.8 mth^{-1} (data from Halbert et al., 1983) to 13.7 mth^{-1} (data from Hoffmann et

al., 1981). A uniform distribution was assumed for the maximum specific growth rate with a minimum value of 11.5 mth^{-1} and a maximum value of 14.5 mth^{-1} .

Solubility Constants

The solubility constants for basaluminite and iron hydroxide were taken from literature values (Dubrovsky et al., 1985). The assumed lognormal distributions for the solubility constants are consistent with the laboratory studies of Lasaga (1984), which indicates orders of magnitude variation as a function of pH.

The distributions of the solubility constants (geometric mean, geometric standard deviation, minimum and maximum) are as follows: log basaluminite (22.7, 1.02, 21.7, and 23.7); and iron hydroxide (3.98×10^1 , 3.16, 1.27, 1.27×10^3). The basaluminite solubility constants are presented as Logs in order to reduce computational problems associated with very large numbers.

The natural variability in ferric hydroxide solubility represents a large uncertainty that cannot be significantly reduced with our current understanding. This results from the probable formation of amorphous iron hydroxide in the mill and the subsequent formation of more crystalline forms as the tailings weather. These different solids have two to three orders of magnitude different values for solubility constants. The use of basaluminite to describe aluminum solubility was based on field data presented by Dubrovsky et al. (1985). It is likely that the chemistry of aluminum is more complex than simple solubility control by basaluminite. Other kinetic factors that are not considered here may be responsible for the uncertainty in aluminum chemistry. Such factors include the dissolution of other aluminosilicates such as clays.

The solubility of basaluminite and iron hydroxide affects the porewater pH; when they are depleted, their absence allows for a substantial change in the porewater pH. This in turn affects the rate of pyrite oxidation (i.e.

oxidation kinetics).

Chemical Rate Constant

The acid flux is sensitive to variations in the value of the chemical rate constant. The chemical rate constant, KCONST, was calculated to be 2.3×10^6 mol.m⁻².mth⁻¹.atm⁻¹ from experimental data (McKay and Halpern, 1958). Further work is required however, over wider ranges of pH. The parameter was assumed to have a triangular distribution with a minimum of 1.18×10^5 , a mode of 2.3×10^6 , and a maximum of 4.72×10^7 mol.m⁻².mth⁻¹.atm⁻¹.

The chemical rate constant directly affects the oxidation kinetics.

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The objective of this project was ... "to provide estimates of the upper and lower limits of rate and quantity of acid generation by the bacterially-assisted oxidation of pyrite and other sulphide minerals in uranium mill tailings". For this study, acid generation is defined as the flux of total acidity per unit time frame (e.g., a month or year) from a unit area of tailings. Total acidity is taken as equivalent to the CO_2 -acidity titration endpoint. Hence, total acidity is defined as the amount of base which would be required to neutralize free protons, all species of aluminum and iron (III), and carbonic acid to this endpoint.

The approach taken in this project was to develop a mathematical model which could estimate acid generation over time after tailings deposition. The model was run deterministically to understand the main trend of its calculation of pH, acidity, porewater concentration and solids content over time. It was run probabilistically, using a Monte Carlo sampling strategy, to estimate the upper and lower limits of acid generation for a hypothetical uranium tailings pile. The model calculates acid generation as a function of both tailings characteristics, such as grain size, thickness of unsaturated zone, temperature, depth of tailings mass and time of year; and as a function of such mineralogical characteristics as pyrite content and the content of other minerals (e.g., gypsum, calcite, basaluminite, goethite).

At a more microscale level, the model calculates the rate of acid generation as a function of various kinetic factors and the gaseous oxygen diffusion coefficient. Kinetic factors include the chemical rate of oxidation and the bacterial rate of oxidation. The oxidation rates are computed as a function of several factors including temperature, oxygen concentration and pH, and, in the case of bacterial oxidation, as a function of bacterial population density, pyrite surface area, carbon dioxide and nutrient levels. The model also includes mass balance equations for solute transport of various chemical species, equilibrium (or kinetically-controlled dissolution) for the various minerals, and electroneutrality equations to calculate solution pH. Some of



these various kinetic and diffusional properties are related to bulk tailings characteristics (e.g., diffusion as a function for moisture content, which is a function of the capillary fringe height and residual moisture content) while others are independent of bulk tailings characteristics (e.g., chemical activity coefficients, solubility constants).

The model has approximately 173 coefficients which require calibration. Here the term, 'calibration' is defined as the selection of a nominal value and/or definition of a probability distribution for each coefficient. The majority of the coefficients are calibrated using literature data (e.g., solubility constants) while the remainder are site specific (e.g., capillary fringe depth, initial pyrite content, rainfall rate). Certain parameters such as infiltration rate, air and ground temperature were varied on a monthly basis but not on an annual basis.

Model Validation Study

Selected results from field investigations at one of the uranium tailings sites in Elliot Lake were used to validate the predictive capability of the acid generation model. Nominal values of coefficients were used to estimate initial characteristics. The model was run for a twenty year simulation period and the predicted results were compared to measured field data obtained approximately 20 years after tailings disposal ceased. The comparison was made for nine output parameters on two sets of data representing quite different tailings characteristics. Based upon these results, the following points are noted:

1. The predicted dissolved sulfate and iron concentrations were in excellent agreement with those observed.
2. The predicted dissolved calcium and aluminum concentrations showed less favourable but acceptable agreement with measured data. The model overpredicts the rate of basaluminite dissolution and slightly underpredicts the aqueous calcium concentration.

3. Overall, excellent agreement was found between predicted and measured pH values over the entire depth profile at the two sampling sites, with exception of the near surface levels.
4. The predicted oxygen profiles closely parallel field measurements on both data sets.
5. Reasonable agreement was found between measured and predicted values of the water contents in both coarse tailings and slime fractions.
6. The residual pyrite content of the tailings after 20 years of leaching was predicted with an acceptable level of accuracy.
7. The predicted and observed locations of the depletion front of calcite were in close agreement.
8. The period in which biological oxidation dominates is short; approximately two to three years over which time basaluminite equilibrium controls pH levels.

Overall, it is concluded that model predictions show good agreement with field observations. Considering that the initial composition of the tailings and other tailings characteristics were not known precisely and that the model parameter values were not adjusted to improve the level of agreement between predicted and observed data, the comparative study is judged to provide substantial confidence in the predictive capability of the reactive tailings assessment model (RATAP).

Probabilistic Simulation Study

A probabilistic simulation was undertaken to assess the limits on the acid flux from the hypothetical tailings example. Based upon these results, the following statements are made:



- 1) For the tailings area simulated in this study, the model calculated that the acid flux decreases fairly rapidly for approximately a decade after tailings disposal. After this period the rate of decline in the flux is much slower and reaches a quasi-steady state rate.
- 2) The maximum yearly acid flux for a tailings with a water table depth of 2.0 m occurred during year two and had a mean of $250 \text{ mol.m}^{-2}.\text{mth}^{-1}$. With time the mean flux reached a quasi-steady state value of about $80 \text{ mol.m}^{-2}.\text{mth}^{-1}$.
- 3) The upper and lower limits of acid generation were found to be typically three times and one quarter of the mean rate respectively.

Sensitivity/Uncertainty Study

The predictions of the model to changes in the magnitude of the model input parameters were assessed to identify those parameters which have the greatest influence on the model predictions. Based on this assessment, the following key statements are made.

- 1) The acid flux is sensitive to variations in the chemical rate constant, the energy of activation, bacterial population density, the initial contents of aluminum hydroxide, calcite and pyrite, the solubility constants for basaluminite and iron hydroxide, the air entry value, residual water content, porosity and the infiltration rates.
- 2) The rate of pyrite oxidation is sensitive to all of the aforementioned input parameters, with the exception of infiltration rates.

Recommendations

The results of the study suggest that further work is warranted in three key

areas. They include:

- 1) Comparison of RATAP model predictions against a wider spectrum of field data to gain additional confidence in the model.
- 2) Investigation of the geochemical mechanisms which control aluminum dissolution under acidic conditions. In this study, it was assumed that the dissolved aluminum concentration is controlled by pH and is in equilibrium with basaluminite. The assumption of the mineral phase is based upon field data which suggests that the porewater is in equilibrium with this phase. With this assumption, the calculated pH is in agreement with field data, but the calculated aluminum concentration appears to be too high. A previous study assumed equilibrium with silica and kaolinite. This assumption gave reasonable calculated values for aluminum, but values for pH which were too high.
- 3) Collection of additional data on the parameters which were shown to be most important and which have a high level of uncertainty associated with them. The sensitivity analysis suggests priorities for research. The priority list however changes with the time after tailings placement. During the initial decade after tailings placement, factors which affect the chemical and biological rate constants were found to be of equal or more importance than factors which affect the infiltration rate and the gaseous diffusion coefficient of oxygen. However, after approximately a decade, factors affecting these physical parameters of gaseous diffusion coefficients become of equal or greater importance than the kinetic parameters.

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APPENDIX A: INITIAL INVENTORY(MODULE I)

A.1 Theoretical Background

A.1.1 Introduction

Before the various modules can be employed the calculation of initial conditions is required. These conditions include: soil temperature, water content, aqueous and solid phase concentrations and the initial pH.

A.1.2 Soil Temperature

The temperature of soil varies with depth and season of the year. It is controlled by solar radiation adsorption, soil thermal properties and meteorological variables such as snow cover, wind and rainfall (Grenier and Bigu, 1983). As shown in Appendix B, Sections B.2.2 and B.2.3, the temperature of the soil can have a significant effect on the chemical and bacterial rates of pyrite oxidation. In addition to influencing the aforementioned rates, the presence of a frozen boundary can also act as a resistance to the transport of oxygen into the soil by reducing the soil-air content.

Several models have been developed that approximate soil temperature from surface meteorological data (Goodrich, 1978; Hayhoe, et al., 1983; Ouellet, 1973). In the model developed by Goodrich (1978) and later adapted by Hayhoe et al. (1983), a heat conduction equation is solved using a centered-difference formulation and Gaussian elimination. Unfortunately, the high level of sophistication in the model is also accompanied by a great deal of data manipulation and computer processing time (Grenier and Bigu, 1983).

Ouellet's (1973) approach is based upon a regression analysis of soil temperature data originating from forty-one Canadian stations. The equation takes the following form:

$$T_s(Z) = b_0(Z) + b_1(Z) X_1 + b_2(Z) X_2 + \dots + b_8(Z) X_8 \quad (A.1.1)$$



where ΔX = the depth of the zone under study (m)
 Q_{rain} = the rate of water application onto the soil from all sources
 (m.hr⁻¹)
 E = the evaporation rate (m.hr⁻¹)
 D_p = the deep percolation rate (m.hr⁻¹)
 R = the rate of lateral movement of water across the soil surface
 as runoff (m.hr⁻¹)
 N_w = soil water content (m³.m⁻³)

The deep percolation rate, D_p , is calculated from the following equation which is based on work by Jury et al., (1976):

$$D_p = (n_w \Delta X^{C6} C5 / \Delta X) \quad (A.1.3)$$

The parameters $C5$ and $C6$ are derived by forcing the deep percolation rate to equal the hydraulic conductivity of the soil, K_{fc} (m.hr⁻¹), at $n_w = n_{fc}$ and to equal the saturated hydraulic conductivity, K_s (m.hr⁻¹), at $n_w = n_t$. The field capacity, n_{fc} (m³.m⁻³), is the volumetric content of water the soil may retain by surface tension. The parameter n_t is the saturated water content of the soil which is equal to the porosity and the parameters $C6$ and $C5$ are given by:

$$C6 = \text{LN} (K_s / K_{fc}) / \text{LN} n_t / n_{fc} \quad (A.1.4)$$

$$C5 = K_s n_t / (n_t \Delta X)^{C6} \quad (A.1.5)$$

Examples of numerical techniques used to simulate the transient behaviour of water in the unsaturated zone and hence determine the water content are found in Hillel (1977), Bresler and Hanks (1969), Kirda et al., (1973), Hanks and Bowers (1962) and Gupta et al., (1977).

determine n_w as a function of height above the water table. The relationship given in Hillel (1980) for the unsaturated zone is:

$$n_w = (h_e/h)^\lambda (n_t - n_r) + n_r \quad (\text{A.2.2})$$

where

- h_e = the height above the water table at which air entry can occur by gravity drainage (m)
- n_t = the maximum water content (= porosity) ($\text{m}^3_{\text{void}} \cdot \text{m}^{-3}_{\text{tailings}}$)
- n_r = the residual water content ($\text{m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$)
- n_w = the water content of the tailings ($\text{m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$)
- h = height above water table (m)
- λ = soil coefficient; is the material dependent constant that is referred to as the grain size distribution parameter

The value of n_w ranges from the value of total porosity (fully saturated) to a residual moisture content that is the minimum value due to gravity drainage. For the purposes of this model, a sand fraction and a slime fraction have been used to represent the two end members of tailings types size distribution. For the sand fraction, $\lambda = 0.68$ and for the slime fraction, $\lambda = 0.78$.

Although transient behaviour of n_w values occur in response to infiltration, it is assumed that the n_w profile will remain at steady state over the long-term. The value of n_a , that is the difference between the total porosity (n_t) and n_w is then used to calculate D_e for any depth in the tailings.

In the saturated zone the water content is set equal to the porosity:

$$n_w = n_t \quad (\text{A.2.3})$$

A.2.3 Initial Solid Phase Concentrations

The initial solid phase concentrations are calculated using the following expression:

A.2 Algorithm Development

A.2.1 Soil Temperature

The model selected to predict the soil temperature profile is based upon theoretical considerations and the experimental data of Grenier and Bigu (1983):

$$T(X,t) = T_m + A_0 [\sin(w \cdot (t-\ell) - X/d)] \exp(-X/d) \quad (A.2.1)$$

where

A_0 = empirical coefficient ($^{\circ}\text{K}$)

w = radial frequency = $2\pi/12$ mth (mth^{-1})

d = dampening depth (m)

X = actual depth of layer (m)

T_m = yearly mean temperature ($^{\circ}\text{K}$)

t = time period (mth)

ℓ = phase-shift constant; a function of the month that represents
 $t = 1$ (mth)

$T(X,t)$ = soil temperature at depth X at time t ($^{\circ}\text{K}$)

The yearly mean temperature for the Elliot Lake area is 277.4°K (Environment Canada, 1981).

After comparing the predicted results against field measurements at a uranium tailings disposal site near Elliot Lake, Ontario, the values of A_0 , T_m , ℓ and d were set to 20°K , 283°K , 0.1 mth^{-1} and 2.0 m respectively (Grenier and Bigu, 1983). The first month, $t=1 \text{ mth}$, was set equal to April.

The experimental data was for an actual tailings disposal site and hence, is site specific in terms of heat generated during pyrite oxidation.

A.2.2 Water Content

A simplified empirical relationship based on tailings data is used to

determine n_w as a function of height above the water table. The relationship given in Hillel (1980) for the unsaturated zone is:

$$n_w = (h_e/h)^\lambda (n_t - n_r) + n_r \quad (\text{A.2.2})$$

where

h_e = the height above the water table at which air entry can occur by gravity drainage (m)

n_t = the maximum water content (= porosity) ($\text{m}^3_{\text{void}} \cdot \text{m}^{-3}_{\text{tailings}}$)

n_r = the residual water content ($\text{m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$)

n_w = the water content of the tailings ($\text{m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$)

h = height above water table (m)

λ = soil coefficient; is the material dependent constant that is referred to as the grain size distribution parameter

The value of n_w ranges from the value of total porosity (fully saturated) to a residual moisture content that is the minimum value due to gravity drainage. For the purposes of this model, a sand fraction and a slime fraction have been used to represent the two end members of tailings types size distribution. For the sand fraction, $\lambda = 0.68$ and for the slime fraction, $\lambda = 0.78$.

Although transient behaviour of n_w values occur in response to infiltration, it is assumed that the n_w profile will remain at steady state over the long-term. The value of n_a , that is the difference between the total porosity (n_t) and n_w is then used to calculate D_e for any depth in the tailings.

In the saturated zone the water content is set equal to the porosity:

$$n_w = n_t \quad (\text{A.2.3})$$

A.2.3 Initial Solid Phase Concentrations

The initial solid phase concentrations are calculated using the following expression:

$$C_{si} = \rho_t X_{fi} / M_{wi} \quad (A.2.4)$$

where

C_{si} = concentration of component i in solid phase (mol.m^{-3})

ρ_t = tailings bulk density (g.m^{-3})

X_{fi} = mass fraction of component i in the tailings (g.g^{-1})

M_{wi} = molecular weight of component i (g.mol^{-1})

A.2.4 Initial Aqueous Concentrations

For the initial inventory, it is assumed that no sulphates have been introduced from pyrite oxidation. Hence, gypsum represents the only source of dissolved calcium and sulphate ions, and the starting concentrations are calculated from equilibrium considerations:

$$[\text{SO}_4^{2-}] = [\text{Ca}^{2+}] = (K_{\text{CaSO}_4} / f_2^2)^{0.5} \quad (A.2.5)$$

where

$[\text{SO}_4^{2-}]$ = concentration of SO_4^{2-} (mol.L^{-1})

$[\text{Ca}^{2+}]$ = concentration of Ca^{2+} (mol.L^{-1})

K_{CaSO_4} = solubility equilibrium constant for CaSO_4 ($\text{mol}^2.\text{L}^{-6}$)

f_2 = activity coefficient for sulphate complexation

Table A.2.1 presents a list of ionic species in the soil water which are assigned an initial value. Also, presented are the ionic concentrations found in the rain water.

A.2.5 Initial pH

The initial pH value is selected to be approximately 0.5 pH units below the expected calculated value. This value is then output to an iterative routine

Table A.2.1

INITIAL IONIC CONCENTRATIONS

<u>Ionic Species</u>	<u>Concentration (mol.L⁻¹)</u>	
	<u>Soil Water</u>	<u>Rain Water</u>
Fe ²⁺	1x10 ⁻⁸	0.0
Fe ²⁺ total	1x10 ⁻⁶	0.0
Fe ³⁺ total	1x10 ⁻⁶	0.0
SO ₄ ²⁺ total	SO ₄ ²⁺	1x10 ⁻⁶
Ca ²⁺ total	Ca ²⁺	1x10 ⁻⁴
Al ³⁺ total	1x10 ⁻¹⁰	0.0
C _{total}	1x10 ⁻³	0.0
NO ₃	0.0	0.0
Potassium	1x10 ⁻³	0.0



which solves for the correct pH value in progressive increasing manner. The initial pH estimate is based upon the particular case (e.g. whether calcite is present or absent) and the time of year. The latter parameter incorporates the variations in the rate of pyrite oxidation. The year is broken in two parts; the first part is defined as January, February, March and December, while the second part is the remaining months.

For cases where calcite is present, (Cases 111 to 114) the initial pH estimate is 6.0 for both time periods. When $AlOH_3$ is present, (Cases 210/220 and 310/320) the initial pH guess is 3.5 for the first part of the year and 3.0, for the second part of the year. When $AlOH_3$ has been depleted (Cases 410/420 and 510/520) the pH estimate is 1.5 for the first part of year and either 0.5 or 1.2 for the remaining months. The 0.5 pH value is employed when pyrite has been depleted from the layer above, but is present in the current layer.

When a layer has been depleted of pyrite the initial pH guess is 5.0. This is based on the observation that the effect of gypsum dissolution is greater than that of aluminum hydroxide:

A.3 Parameters Distributions

The following section describes the parameters which are used to calculate the initial inventories, soil temperatures, water contents and pH. Table A.3.1 lists the probability distribution types and descriptions and the computer source symbol assigned to the parameters.

A.3.1. Capillary Fringe

The capillary fringe, L_c , is a zone located above the water table and below the unsaturated zone. In this zone the pores are saturated, but the pressure heads are less than atmospheric:

To determine the layer at which the capillary fringe is located, the following expression was employed:

$$L_c = L_s - \frac{h_e}{dx} \quad (A.3.1)$$

where

L_c = layer at which the capillary fringe begin

L_s = layer at which the water table is located

h_e = height above water table at which air entry can occur by gravity drainage (m)

dx = thickness of each layer (m)

For this study a triangular probability distribution is employed to describe h_e ; a minimum of -0.05 m, a mode of -0.5 m and a maximum of -1.5 m.

A.3.2 Residual Water Content

The residual water content, n_r , is the volumetric content of water that will not continue to percolate through the soil, but is held to the soil by surface tension. The residue water content is equal to the field capacity at a height above the water table which is not influenced, in terms of moisture content, by the water table.

For this study a normal probability distribution is assumed for the residual porosity with a mean value of $0.08 \text{ m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$ and a standard deviation of $0.01 \text{ m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$. The minimum and maximum values were set at 0.05 and $0.11 \text{ m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{tailings}}$, respectively.

A.3.3 Porosity

The porosity, n_t , is defined as the volume of voids divided by the total unit volume of soil. For unconsolidated deposits, the porosity varies from 25 to 40% for gravel, 25 to 50% for sand, 35 to 50% for a silt and 40 to 70% for clay (Freeze and Cherry, 1979).

In this study the porosity of tailings is assumed to have a triangular probability distribution with a minimum of $0.45 \text{ m}^3 \cdot \text{m}^{-3}$, mode of $0.50 \text{ m}^3 \cdot \text{m}^{-3}$

Table A.3.1
INITIAL INVENTORY MODULE PARAMETERS

Parameter Values						
Symbol	Description	Units	Nominal	Probabilistic	Origin	Computer Code
A_0	Empirical temperature coefficient	(°K)	20	C(20)	Input	AO
d	Dampening depth	(m)	2.0	C(2.0)	Input	D
h_e	Suction head	(m)	-0.5	T(-1.5,-0.5,-0.05)	Input	HE
L	Phase-shift constant	(unitless)	0.1	C(0.1)	Input	COEFF
n_a	Volumetric air content of soil	(m ³ _{air} ·m ⁻³ _{tail})	calculated	calculated	Initial	NA(i)
n_r	Residual water content	(m ³ _w ·m ⁻³ _{tail})	0.08	N(0.08,0.01,0.05,0.11)	Input	NR(i)
n_t	Porosity	(m ³ _{void} ·m ⁻³ _{tail})	0.50	T(0.45,0.50,0.55)	Input	NT(i)
n_w	Water content	(m ³ _w ·m ⁻³ _{tail})	calculated	calculated	Initial	NW(i)
ρ_t	Bulk density of the tailings	(kg·m ⁻³)	1300	C(1300)	Input	BD
T_s	Soil monthly temperatures	(°K)	calculated	calculated	Kinetic	TS(i,m)
T_m	Yearly mean temperature	(°K)	283	C(283)	Input	TAVG
X_{pyr}	Mass fraction of pyrite	(g·g ⁻¹)	0.06	U(0.048,0.072)	Input	XPYR
X_{gyp}	Mass fraction of gypsum	(g·g ⁻¹)	0.05	U(0.04,0.06)	Input	XGYP
X_{FeOOH}	Mass fraction of ferric hydroxide	(g·g ⁻¹)	0.0041	U(0.0025,0.0057)	Input	XFE00H
X_{AlOH3}	Mass fraction of basaluminate	(g·g ⁻¹)	0.0023	U(0.0014,0.0032)	Input	XALOH3
X_{Ser}	Mass fraction of sericite	(g·g ⁻¹)	0.136	U(0.11,0.16)	Input	XSER
X_{cal}	Mass fraction of calcite	(g·g ⁻¹)	0.0005	U(0.000,0.001)	Input	XCAL
λ	Soil coefficient for moisture content	(unitless)	0.73	U(0.68,0.78)	Input	LAMDA

NOTE:

i Indicates the particular layer
m Indicates the month of the year

Key to Probabilistic

Parameters Value: C - Constant (single value)
N - Normal (mean, std. dev., min., max.)
T - Triangular (min., mode, max.)
U - Uniform (min., max.)

Table A.3.2

MINERALOGICAL COMPOSITION OF TYPICAL PYRITIC URANIUM TAILINGS²

<u>Primary Minerals</u>	<u>Wt. %</u>	<u>Moles/Tonne</u>
Quartz ¹	64.7	10,800
Sericite ¹	13.6	340
K-Feldspar ¹	3.24	120
Na-Feldspar ¹	1.07	40
Chlorite ¹	0.65	5.8
Gypsum	6.5	375
Pyrite	6.0	500
Calcite	0.05	50
Iron Oxyhydroxides (Fe) ₂ O ₃	0.41	73
Al(OH) ₃	0.23	30
<u>Misc. Elements</u>		
Ba	0.022	1.6
Pb	0.033	1.5
PO ₄ , Zn, Co, Cu, Ni, Ti, Y, F, Th, U, impurities	3.0	----
<u>Misc. Precipitates</u>		
SiO ₄ (am)	0.036	6.0
SnO ₄	<0.01	0.14
PbSO ₄	<0.01	0.07
BaSO ₄	<0.01	0.0005
	100	

Note

1. Sericite, feldspar and chlorite are present in ore. The exact content is not well known. Levels given are based upon mass balance calculations of potassium, sodium, magnesium, aluminum and residual silica (total-quartz).
2. Adapted from Beak (1985) with modifications.

and a maximum of $0.55 \text{ m}^3 \cdot \text{m}^{-3}$.

A.3.4 Tailings Density

The average specific gravity of uranium tailings is $2700 \text{ kg} \cdot \text{m}^{-3}$ and is not subject to great variation as the primary component ($> 60\%$) of the tailings is quartz. The bulk density or weight of tailings solids per cubic metre of tailings however is highly variable. Values in slimes ponds have been measured as low as $0.5 \text{ t} \cdot \text{m}^{-3}$ while stacks of coarse materials have been measured at more than $1.6 \text{ t} \cdot \text{m}^{-3}$. The primary factors affecting bulk density are the grain size, gypsum content, method of tailings placement, and moisture content.

For typical Sulphidic uranium tailings an average bulk density of $1.3 \text{ t} \cdot \text{m}^{-3}$ was assumed. The range of densities is expected to be normal with a standard deviation of $0.1 \text{ t} \cdot \text{m}^{-3}$.

A.3.5 Mineralogy/Chemical Composition

Sulphidic uranium ores from the Elliot Lake area consist of a quartz pebble conglomerate with sericite and pyrite. The mineralogical composition of the tailings is variable. The estimated composition, mass fractions (X_f), of the primary minerals and those minerals which are likely to control the chemical composition of the tailings porewater are summarized in Table A.3.2.

As previously stated, the major component is quartz which typically comprises in the order of 70 percent of the ore. The total silica content is in the range of 78 percent and includes minerals such as sericite, feldspar and chlorite.

The composition of pyrite in the tailings (X_{pyr}), varies from site to site. The sulfides of iron (pyrite and pyrrhotite) can constitute as much as some 35% of the solid fraction (Halbert, et al, 1983). For typical pyritic uranium tailings a $6\% \text{ kg} \cdot \text{kg}^{-1}$ pyrite fraction has been reported (Beak, 1985). This



nominal value was employed in the model. The variability in this parameter is assumed to be $\pm 20\%$ and is described as being uniformly distributed.

A.4 Algorithm Calibration Validation

In the following section, predicted soil temperature versus depth profiles and water content versus depth profiles are compared against experimental data.

A.4.1 Temperature Profiles

In Figures A.1 to A.5, monthly temperature variations at various depths (0.1, 0.2, 0.5, 1.0, and 1.5 m) are presented. The predicted temperatures closely resemble the field observations by Grenier and Bigu (1983).

The model's results and the field observations both show a reduction in the temperature variation with depth (seen as an amplitude reduction in the sine wave) and an increasing time lag between the maximum surface temperature and the peak temperature at depth (seen as a shift in the sine wave to the right).

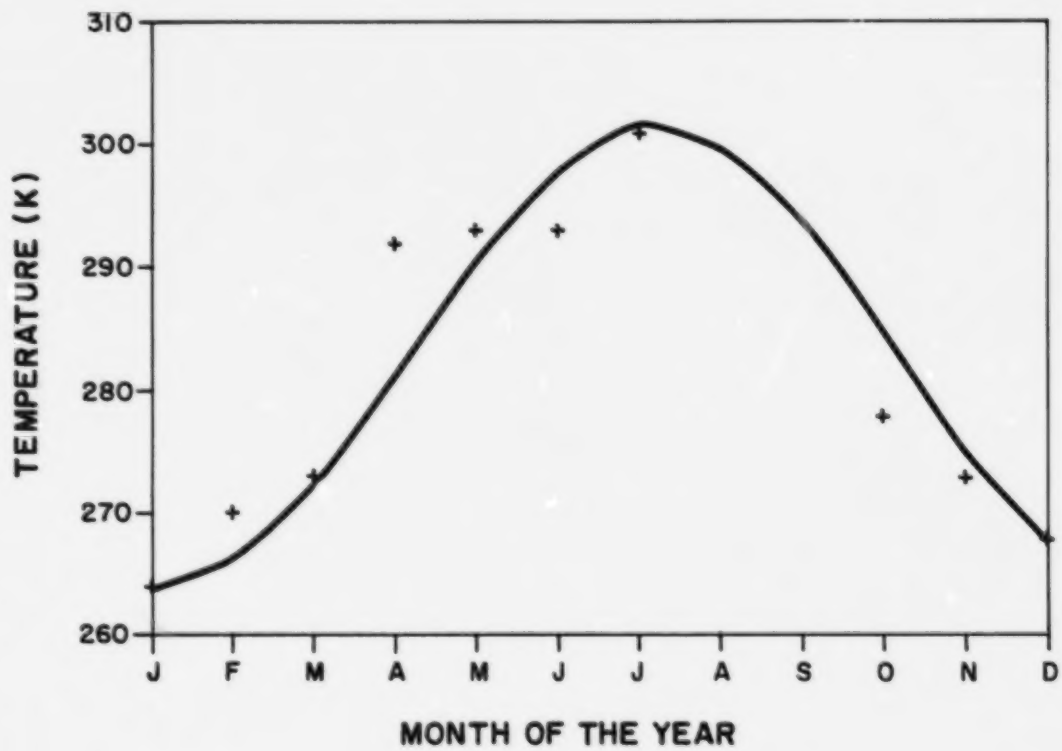
A.4.2 Water Content

In Figure A.6 a profile of water content, n_w , determined by field measurements, Smyth (1981), is presented. The field measurements are for the Nordic tailings. During sampling it was observed that "fine-sand" material was present to a depth of approximately 2.35 m and at a depth greater than 2.6 m a "silty sand" was observed. The water table depth was approximately 4.0 m.

Figure A.6 also shows the model's prediction of water content. In the simulation, the characteristics of a "fine-sand" soil, see Table A.4.1, were used to a depth of 2.6 m and the characteristics of a silty sand were used for the remaining layers.

The observed data indicates that a front of water, caused by a rain event, may be moving through the soil. The model is unable to predict this unsteady state water migration and hence does not predict the high water contents at the water front.

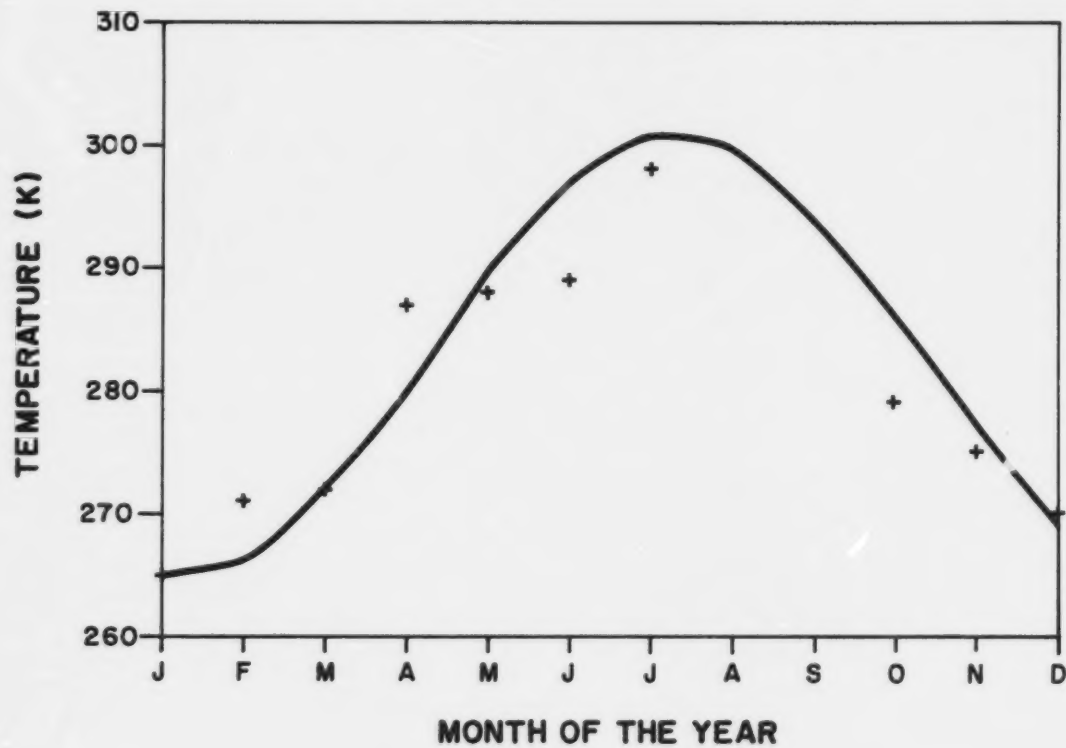
FIGURE A.1
MONTHLY TEMPERATURE VARIATIONS
AT 0.1m DEPTH



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF GRENIER AND BIGU (1983)

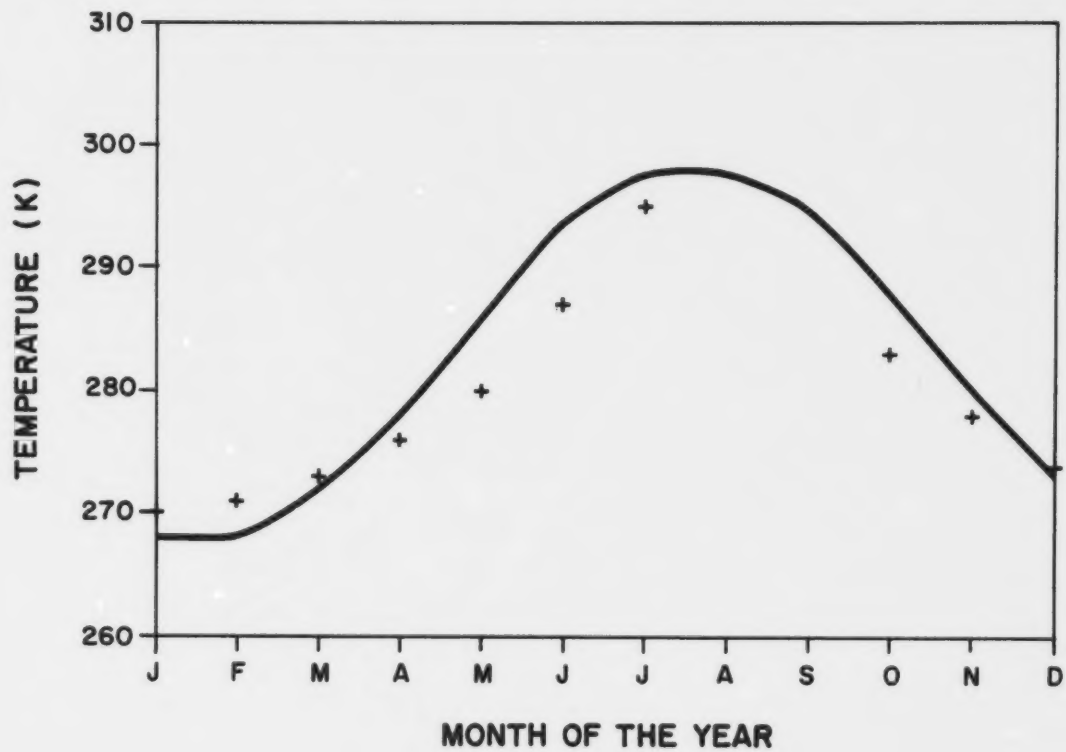
FIGURE A.2
MONTHLY TEMPERATURE VARIATIONS
AT 0.2m DEPTH



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF GRENIER AND BIGU (1983)

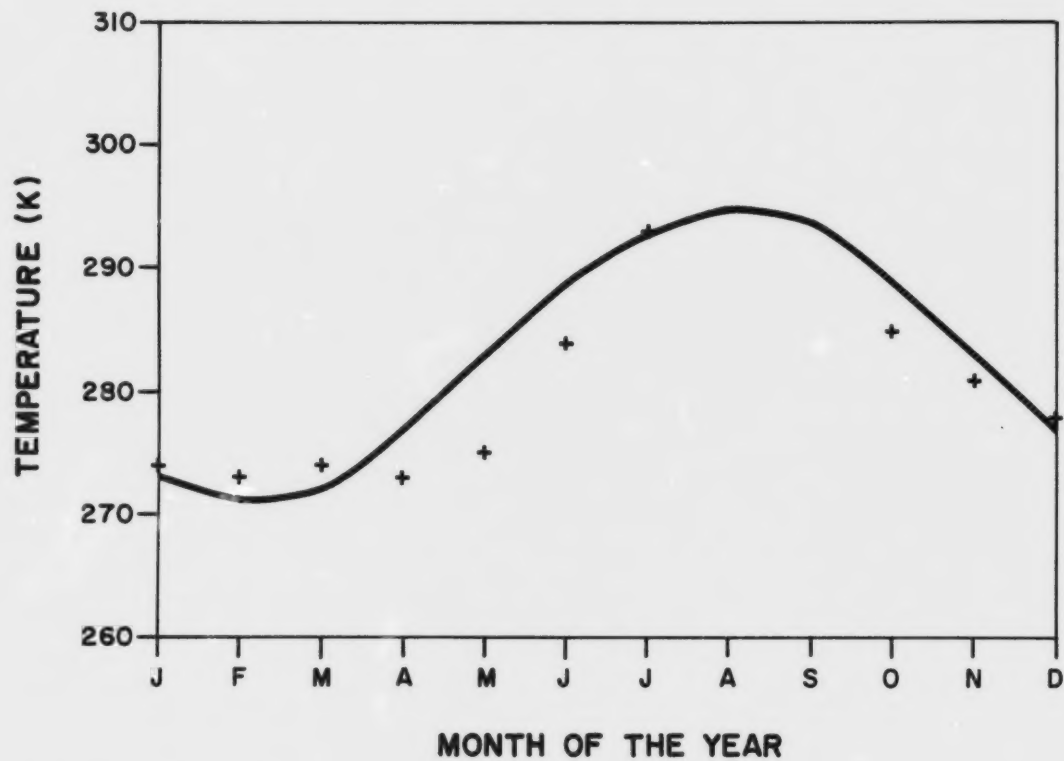
FIGURE A.3
MONTHLY TEMPERATURE VARIATIONS
AT 0.5m DEPTH



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF GRENIER AND BIGU (1983)

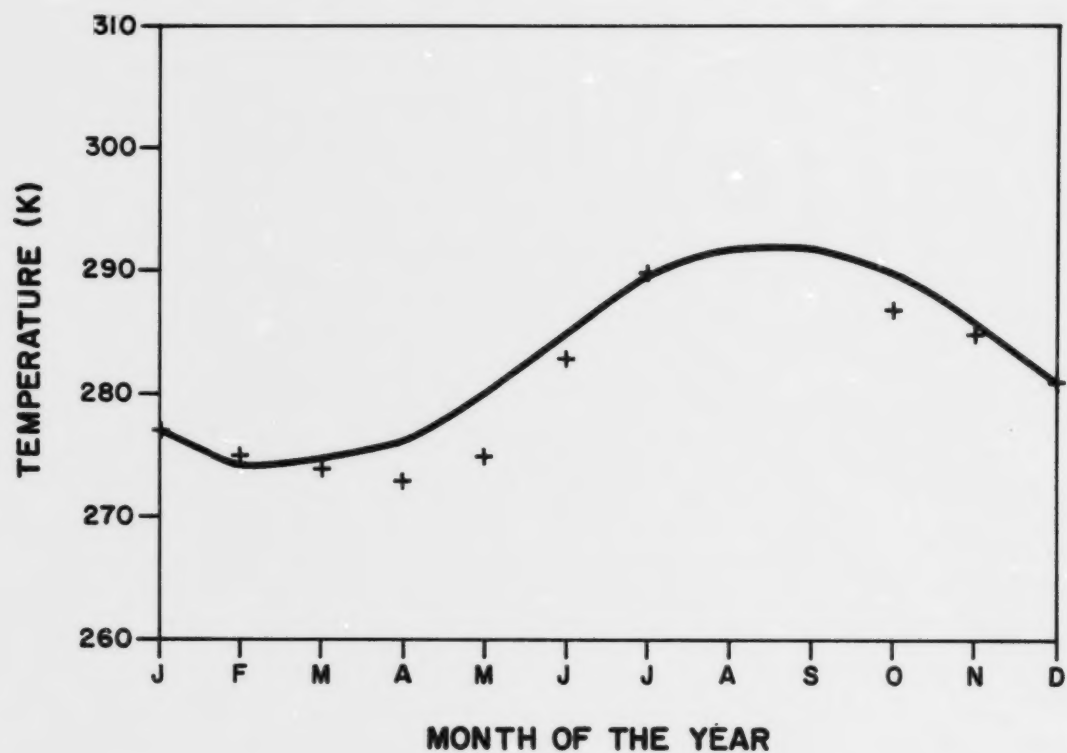
FIGURE A.4
MONTHLY TEMPERATURE VARIATIONS
AT 1.0m DEPTH



LEGEND :

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF GRENIER AND BIGU (1983)

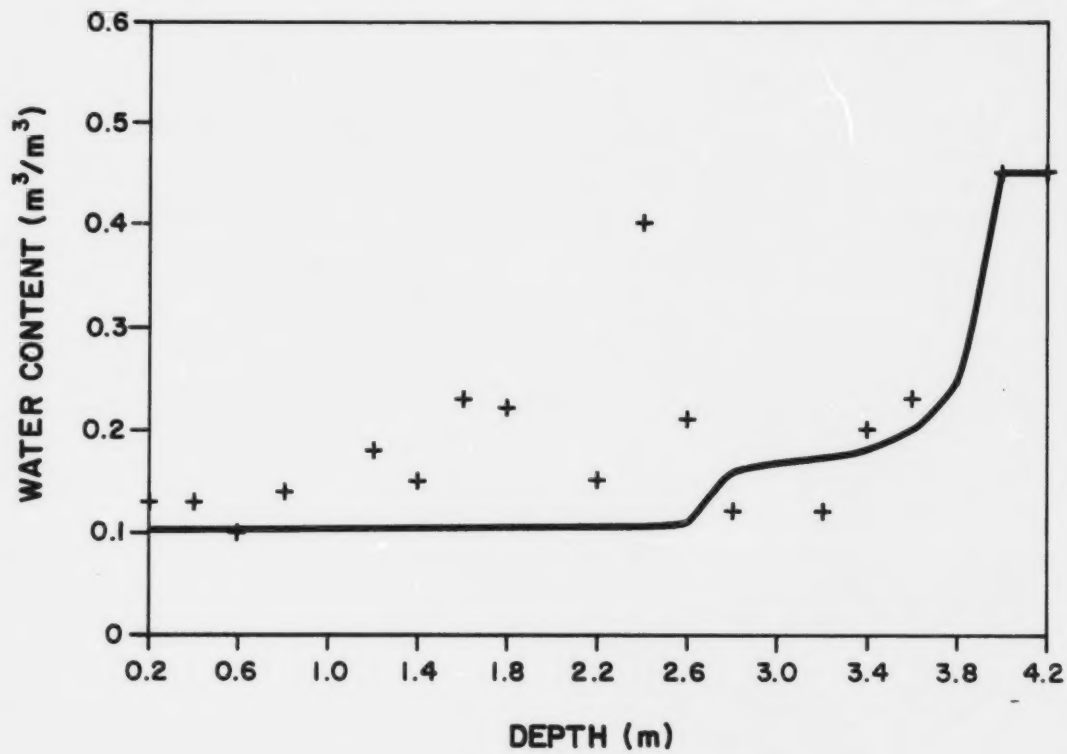
FIGURE A.5
MONTHLY TEMPERATURE VARIATIONS
AT 1.5m DEPTH



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF GRENIER AND BIGU (1983)

FIGURE A.6
WATER CONTENT
AS A FUNCTION OF DEPTH
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF SMYTH (1981)

Table A.4.1

PARAMETERS INFLUENCING WATER CONTENT

<u>Parameter</u>	<u>Units</u>	<u>Soil Type</u>	
		<u>Fine Sand</u>	<u>Silty Sand</u>
h_e	m	-0.1	-0.5
n_t	$m^3.m^{-3}$	0.4	0.45
n_r	$m^3.m^{-3}$	0.10	0.08
λ	unitless	0.68	0.73

The observed data indicates that a front of water, caused by a rain event, may be moving through the soil. The model is unable to predict this unsteady state water migration and hence does not predict the high water contents at the water front.

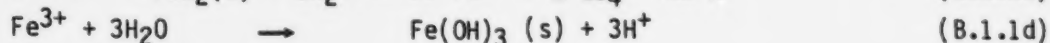
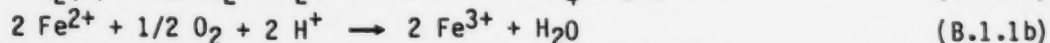
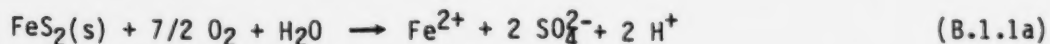
APPENDIX B: KINETICS (MODULE II)

B.1 Theoretical Background

B.1.1 Introduction

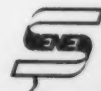
The oxidation of pyritic minerals results from both chemical and bacterial attack. Pyrite oxidation has conclusively been shown to be catalyzed by the presence of iron- and sulphur-oxidizing bacteria. It is most significant at acidic pH's.

Bacteria-assisted oxidation of pyrite involves both direct and indirect contact mechanisms. The direct contact mechanism entails enzymatic oxidation of the insoluble sulphide moiety. In contrast, the indirect mechanism involves bacterial oxidation of the dissolved ferrous component to the ferric state. The ferric iron, in turn, acts as the primary oxidant of pyrite and is reduced to ferrous iron. The re-oxidation of the dissolved ferrous component which is catalyzed by bacterial activity, completes the cyclic process. The overall oxidation can be expressed by the following stoichiometric equations:



Equation (B.1.1a) represents the overall reaction stoichiometry for pyrite oxidation to ferrous iron and sulphate. Equations (B.1.1b) and (B.1.1c) reflect mechanistic sequences, equation (B.1.1b) being mediated by bacteria while equation (B.1.1c) is the abiotic dissolution of pyrite by Fe^{3+} . Ferric iron solubility is a function of pH as indicated by equation (B.1.1d).

A number of factors have been shown to affect the rate of oxidation of pyritic material including:



- i) the geochemistry of the pyritic material;
- ii) the amount of pyrite present in the waste material and the exposed surface area of the pyritic component;
- iii) the availability of oxygen which is the principal electron acceptor;
- iv) the availability of carbon dioxide which is the sole source of carbon for the strictly chemolithotrophic bacteria of interest;
- v) the pH of the aqueous phase (e.g. tailings porewater);
- vi) the temperature of the aqueous phase (e.g. tailings porewater temperature);
- vii) the availability of nutrients, in particular phosphorus; and
- viii) the presence (or absence) of organic inhibitors.

Documentation on the influence of the factors affecting oxidation of pyritic uranium tailings has been largely completed in previous work; for a review of bacteria-assisted oxidation see SENES (1984), while for chemical oxidation see Lowson (1982).

B.1.2 Microbial Oxidation

Bacterial activity has been found to increase the rate of oxidation of pyrite material several times over that which is attributable solely to chemical oxidation in an acid environment. Of the various species that have been isolated from pyritic soils, Thiobacillus ferrooxidans plays the most significant role in the formation and propagation of acidic conditions.

For the typical acid conditions found in pyritic tailings porewaters, the rate of pyrite oxidation can be expressed in terms of bacterial oxidation as follows:

$$R = \frac{-1}{A} \frac{dN_p}{dt} = \frac{-1}{Y_{x/s}} \frac{dX_p}{dt} \quad (B.1.2)$$

where

R = the specific reaction rate (mol.m⁻² pyrite surface.mth⁻¹)

Y_{x/s} = growth yield coefficient (g biomass.mol⁻¹ pyrite)

X_p = bacterial population density (g biomass. m^{-2} pyrite surface area)

A = the surface area of the pyrite (m^2)

N_p = amount of pyrite (mol)

t = time (mth)

The above equation can be expressed in terms of the bacterial specific growth rate by normalizing with regard to bacterial population density. Hence:

$$\frac{Y_{X/S}}{A} \frac{1}{X_p} \frac{dN_p}{dt} = \frac{1}{X_p} \frac{dX_p}{dt} = \mu \quad (B.1.3)$$

where

μ = the specific growth rate (mth^{-1}).

The specific rate of pyrite oxidation then, is:

$$R = \frac{-\mu X_p}{Y_{X/S}} \quad (B.1.4)$$

Monod (1942 and 1950) kinetics can be used to relate the specific growth rate of the microorganisms to substrate concentration, as:

$$\mu = \mu_{max} \frac{S}{K_m + S} \quad (B.1.5)$$

where

μ_{max} = maximum growth rate (mth^{-1})

K_m = the half saturation content, i.e. the concentration of substrate supporting a growth rate equal to one-half the maximum growth rate ($\mu_{max}/2$), ($mol \cdot m^{-3}$)

S = amount of substrate per volume of tailings ($mol \cdot m^{-3}$)

Combining equations (B.1.2) and (B.1.5) into an overall rate of pyrite oxidation equation results in:



$$R = \frac{-1}{A} \frac{dN_p}{dt} = \frac{-X_p}{Y_{x/s}} \left(\frac{\mu_{\max} S}{K_m + S} \right) \quad (\text{B.1.6})$$

The coefficients of the Monod equation (B.1.5), k_m and $\mu_{\max}$ can be evaluated by rearranging the expression to form the Lineweaver-Burk equation:

$$\frac{1}{\mu} = \frac{K_m}{\mu_{\max}} \frac{1}{S} + \frac{1}{\mu_{\max}} \quad (\text{B.1.7})$$

This linearized form, equation (B.1.7), has been most often used (Gale and Beck, 1967; Silver and Lundgren, 1968; Schnaitman et al., 1969; MacDonald and Clark, 1970; Wong et al., 1974; Tomizuka et al., 1976; Eccleston and Kelly, 1978; Kelly and Jones, 1978; DiSpirito and Tuovinen, 1982; Brown and Forshaug, 1983) to evaluate the constants from laboratory systems.

Unfortunately, the specific growth rate, μ , is a function of several parameters which are not explicitly included in any of the above equations. The parameters include pH, temperature, oxygen concentration, carbon dioxide concentration, nutrient level, water content, toxicants and inhibitors. The influence of these parameters on the specific growth rate are reviewed below for the purpose of defining mathematical expressions which can be included in the acid generation model. The effect of a limiting oxygen concentration is discussed in Appendix D.

Carbon Dioxide

Carbon dioxide is the main carbon source used by autotrophic thiobacilli for growth. The importance of carbon dioxide as a limiting nutrient is dependent on the geochemistry of the waste material. If the waste material contains a calcareous component, then an ample supply of CO_2 should be available (Harries and Ritchie, 1983). However, in the case of uranium tailings which have undergone an acid leach in the mill, the only significant source of carbon dioxide is likely to be that available in the air mass diffusing into the tailings pore space unless limestone has been purposely added to the tailings to control acidification (SENES, 1984).

The efficiency of carbon dioxide fixation by T. ferrooxidans during cell growth was measured to equal about 1 μ mole of carbon dioxide for each 100 μ moles of ferrous iron oxidized (Beck, 1960).

Several researchers have found that bacterial activity can be increased by raising the carbon dioxide content in the gas phase. Torma et al. (1972) observed that the optimum carbon dioxide content in the gaseous phase, was about 0.22 percent, over the range of 0.03 to 7.92 percent. At CO₂ contents above 0.22 percent, there was no further increase in bacterial growth rate occurred. Approximately a two-fold increase in the leach rate was measured as the carbon dioxide content was increased from 0.03 to 0.22 percent.

In a study by Hoffmann et al. (1981) the reaction rate increased with increasing partial pressure of CO₂ (see Table B.1.1), results which are similar to the data of Torma et al. (1972). There was only a nominal increase in the rate of reaction in these experiments at partial pressures greater than 0.23 percent.

Little information exists in the literature on the effect of very low fluxes of carbon dioxide on bacterial activity. Oxidation of pyritic material has been shown to proceed in the laboratory under conditions where there is a low carbon dioxide content in the gaseous phase. The rate of oxidation however, was much slower than observed with no restriction on carbon dioxide (Kelly and Jones, 1978).

pH

T. ferrooxidans, the main bacteria catalyzing pyrite oxidation has an optimum growth rate in the acidic pH range (i.e. pH 1.5 to 5.0) (SENEs, 1984). In studies by Arkesteyn (1979) the rate of bacterial oxidation of pyrite by Thiobacillus ferrooxidans was observed to be a maximum over a pH range from 3.0 to 3.5. The work of Silverman and Lundgren (1959a), Landesman et al. (1966), and Malouf and Prater (1961), suggest that the maximum activity falls in the pH range between pH 2.5 and 4.0. The particular range of pH over which the growth of T. ferrooxidans is optimized is a function of the type of

substrate (SENES, 1984).

Jaynes et al. (1984) fitted a quadratic equation to the pH data given by Silverman and Lundgren (1959a) and Schnaitman et al. (1969) for the pH range $1.54 < \text{pH} < 4.95$. It is:

$$X_{\text{pH}} = -0.35 \text{ pH}^2 + 2.3 \text{ pH} - 2.7 \quad (\text{B.1.8})$$

where

X_{pH} = fraction of peak cell activity as influenced by pH (0 to 1)

The maximum cell activity ($X_{\text{pH}} = 1.0$) occurs at $\text{pH} = 3.25$ in this function.

Nutrients

Nutrient requirements (such as nitrogen and phosphorus) for T. ferrooxidans are usually not limiting as extremely small concentrations are quite sufficient for growth (Nordstrom, 1982). Tuovinen and Kelly (1973) observed that T. ferrooxidans grow in the absence of any added N compound and suggested that they may fix atmospheric nitrogen.

Hoffmann et al. (1981) carried out experiments to determine the optimal N/P ratio for maximum acceleration of the rate of leaching and minimum inhibition by phosphate complexes and precipitates. As the N/P molar ratio was increased initially, the leaching rate increased until a maximum was reached at an N/P ratio equal to approximately 90 to 1. Above this ratio, the reaction rate decreased to a steady value at molar ratios greater than approximately 150 to 1.

Temperature

Investigators have reported the optimum temperature for ferrous iron oxidation by T. ferrooxidans to lie between 33 and 40°C (Malouf and Prater, 1961; Landesman et al., 1966; MacDonald and Clark, 1970). Leaching studies on metal sulphide ores and concentrate samples have demonstrated that the optimum

Table 8.1.1

REACTION RATE DEPENDENCE ON
THE PARTIAL PRESSURE OF CARBON DIOXIDE

<u>Exp</u>	<u>Carbon Dioxide Partial Pressure (atm)</u>	<u>Rate of Dissolution (mg.L⁻¹.d⁻¹)</u>
A	3.2×10^{-4}	124.0
A control	3.2×10^{-4}	20.8
B	1×10^{-3}	142.0
B control	1×10^{-3}	25.0
C	1.0×10^{-2}	144.0
C control	1.0×10^{-2}	23.3
D	0.1	162.0
D control	0.1	21.0

Note

Conditions; $43 \mu\text{m} < \text{Particle Diameter} < 74 \mu\text{m}$; T. ferrooxidans; pH = 2.5
Control refers to abiological pyrite oxidation

Reference

Hoffmann et al., 1981



temperature generally is in the range of 30 to 35°C (Razzell and Trussell, 1963; Torma et al., 1970).

The rate of reaction increases with increasing temperature within the range tolerated by the organism. This increase is often described by the Arrhenius equation (Lyman et al., 1982):

$$Y = I_r \exp(-E_a/R_g T_a) \quad (B.1.9)$$

where

Y = temperature-corrected rate of reaction (mth^{-1})

I_r = initial rate of reaction (mth^{-1})

E_a = activation energy (cal.mol^{-1})

R_g = universal gas constant ($\text{cal.mol}^{-1}.\text{°K}^{-1}$)

T_a = absolute temperature (°K)

Another approach to describe the temperature dependence is the development of an empirical relationship. Jaynes et al. (1984) developed the following relationship for cell activity over the temperature range of $4^\circ\text{C} < T < 55^\circ\text{C}$ for their laboratory data:

$$X_T = -1.2 \times 10^{-5} T^3 - 4.4 \times 10^{-4} T^2 + 0.066 T - 0.25 \quad (B.1.10)$$

where

X_T = fraction of peak cell activity as influenced by temperature (0 to 1)

T = temperature (°C)

In the equation the peak cell activity ($X_T = 1.0$; $dX_T/dT = 0.0$) was assumed to occur at 32°C , falling to a zero activity ($X_T = 0.0$) at 0°C .

Water Content

The moisture content can be an important variable in determining microbial activity in tailings. Most microorganisms require water because of their relatively permeable cell membranes and large surface-to-volume ratio (Scow, 1982). Conversely, moisture can limit the rate of oxygen transport through



the soil pore space and thus reduce the level of microbial activity.

The measure of soil moisture that is most relevant to describing the effect of water content on microorganisms is not moisture content but "water potential". Water potential is an energy term and can be defined as the difference in free energy between the system under study, soil water, and a pool of pure water at the same temperature (Brock, 1975). The water potential represents the total contributions of gravity, soil matrix, and osmotic pressure (Scow, 1982). The limits of soil water potential on most bacteria are -8×10^6 Pa (-80 bar), as the lower limit, and approximately -5×10^5 Pa (-5 bar), as the upper limit (Gray, 1978).

In a study by Belly and Brock (1974) the activity of T. ferrooxidans in coal refuse materials was measured at different water potentials. The study concluded that T. ferrooxidans resemble many other common soil bacteria in requiring a fairly high water potential for their activity. A minimum water potential for growth of -2.3×10^6 Pa (-23 bars) was observed under conditions analogous to a coal refuse pile (Brock, 1975).

Inhibitors

Several organic and inorganic compounds are known to inhibit T. ferrooxidans activity. Among the most inhibitory compounds are organic and amino acids (Matin, 1978). At organic acid (eg. acetate and butyrate) concentrations as low as 0.1 mol.L^{-1} , the growth of T. ferrooxidans can be inhibited (Matin, 1978).

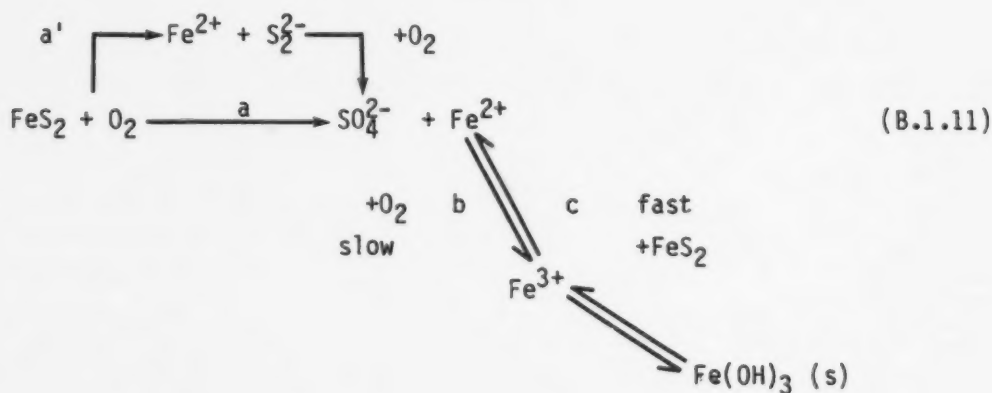
In contrast to most other bacteria, the tolerance of T. ferrooxidans to toxic metal ions is remarkable. Various strains have been reported to tolerate 1 mg.L^{-1} mercury, 50 to 100 mg.L^{-1} selenium, tellurium, and arsenic anions (Brierley, 1978), 200 mg.L^{-1} silver (Sugio *et al.*, 1981a), 0.5 to 1.0 g.L^{-1} uranyl and thorium ions (DiSpirito and Tuovinen, 1982), 2 g.L^{-1} of molybdenum and 5 g.L^{-1} of chromium (Lundgren and Silver, 1980), 10 to 30 g.L^{-1} of aluminum, cobalt, copper, manganese, and nickel (Lundgren and Dean, 1979;

Lundgren and Silver, 1980) and from 70 to 120 g.L⁻¹ of zinc in solution (Torma et al., 1970 and 1972).

Although metal ion tolerance varies with the particular strain and environmental conditions, T. ferrooxidans possess a well noted ability to adapt to increasingly higher metal levels with each successive generation. Some evidence suggests that this adaptability is due to plasmid encoding proteins that render intracellular toxic metals inactive (Torma, 1983). Plasmid Deoxyribonucleic Acid (DNA) has been found in 11 of 15 strains of T. ferrooxidans (Martin et al., 1981). While plasmid was not detected in the other four, it may have been present.

B.1.3 Chemical Oxidation

The chemical mechanisms and chemical reaction kinetics involved in pyrite oxidation are briefly examined below. The following sequence of chemical steps have been proposed for the chemical oxidation reaction path in the context of acid mine drainage (Singer and Stumm, 1968; Singer and Stumm, 1970; Lundgren and Silver, 1980; Nordstrom, 1982).



The above steps can be divided into three essentially different reactions (Lowson, 1982):

- i) the oxidation of pyrite by molecular oxygen to Fe^{2+} and SO_4^{2-} via reaction a or a'. This is viewed as the necessary primary step by Lowson (1982).
- ii) the oxidation of Fe^{2+} to Fe^{3+} by molecular oxygen, step b. Singer and Stumm (1970) regard this as the necessary primary step.
- iii) the oxidation of pyrite by Fe^{3+} , step c. This is viewed as a fast step.

The rate of chemical oxidation can be represented by:

$$R = \frac{-1}{A} \frac{dN_p}{dt} = \frac{-k N_p}{A} \quad (\text{B.1.12})$$

where

- R = the specific rate of chemical oxidation ($\text{mol.m}^{-2}.\text{mth}^{-1}$)
 A = the surface area of the pyrite (m^2)
 N_p = amount of pyrite (mol)
 t = time (mth^{-1})
 k = rate constant (mth^{-1})

Based upon laboratory data, Nicholson (1984) and Nicholson et al. (1986) proposed the following expression for calculating the chemical rate of pyrite oxidation:

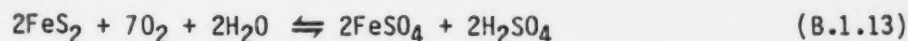
$$\frac{-dN_p}{dt} = w A K_a C A_c \exp(-E_a/R_g T) (1 + K_a C)^{-1}$$

where:

- w = stoichiometric ratio of $\text{FeS}_2/\text{O}_2 = 15/4$
 K_a = adsorption constant of oxygen on pyrite = $1.36 (\text{m}^3.\text{mol}^{-1})$
 A_c = Arrhenius constant = $3.34 \times 10^{10} (\text{mol.m}^{-2}\text{h}^{-1})$
 E_a = energy of activation = $88 (\text{KJ.mol}^{-1})$
 R_g = gas constant = $8.314 (\text{J.mol}^{-1}.\text{°K}^{-1})$
 T = temperature (°K)
 C = concentration of oxygen in the gas phase (mol.m^{-3})

Kinetics of O₂ Oxidation

The overall stoichiometry for oxidation of pyrite by oxygen may be represented as (Lowson, 1982):



The principal reaction, in the absence of mass transport limitations, is a heterogeneous surface reaction involving electron transfer from pyrite to the oxidizing agent, adsorbed oxygen, on the surface (U.S. EPA, 1971). Conditions affecting the rate of chemical oxidation include; temperature, pH, water concentration, concentration of ferric iron, sulfate and other ions, oxygen concentration and surface area. The latter two conditions are discussed in Appendix D.

pH

Below pH 3.0, changes in pH have little effect on the oxidation rate (Smith, Svanks and Shumate, 1968). However, above pH 3.0 the oxidation rate increases, although slowly at first, to the point where the rate doubles for every two pH units above pH of 6.0 (U.S. EPA, 1971).

Smith and Shumate (1970) demonstrated that the rate of reaction for the oxidation of pyrite in water at 25°C and 0.1 MPa oxygen partial pressure increases nonlinearly, as the pH is raised from 1 to 10.

Water Concentration

The role of water is as of yet not clearly understood. In the atom-transfer model of Singer and Stumm (1970), water is relegated to the role of solvent, whereas in the electrochemical model of Bailey and Peters (1976), it is a reactant.



Temperature

The influence of temperature is similar to that of bacterial oxidation; over the range of temperatures comparable to natural conditions, the rate approximately doubles for each 10°C rise (Morth and Smith, 1966; Konecik, 1965).

Kinetics of Fe³⁺ Oxidation

It has been proposed that the rate of reaction is proportional to the fraction of the pyrite surface occupied by the ferric ions (Garrel and Thompson, 1960):

$$\frac{d[\text{Fe}^{3+}]}{dt} = \frac{k[\text{Fe}^{3+}]}{\Sigma[\text{Fe}]} \quad (\text{B.1.14})$$

where

$[\text{Fe}^{3+}]$ = the concentration of the ferric ion ($\text{mol} \cdot \text{m}^{-3}$)

$\Sigma[\text{Fe}]$ = the concentration of iron ($\text{mol} \cdot \text{m}^{-3}$)

k = reaction rate (mth^{-1})

In a study by Smith, Svanks and Halko (1969) the expression for the Fe³⁺ oxidation of pyrite was based upon a competitive adsorption ion model:

$$r = \frac{k \text{ Fe}^{2+}/\text{Fe}^{3+}}{(1/\text{Fe}^{3+} + k_1 + k_2 \text{ Fe}^{2+}/\text{Fe}^{3+})} \quad (\text{B.1.15})$$

where

k = reaction rate constant (mth^{-1})

k_1, k_2 = adsorption equilibrium constants for ferric and ferrous ions ($\text{m}^3 \cdot \text{g}^{-1}$)

$\text{Fe}^{2+}, \text{Fe}^{3+}$ = ion concentrations ($\text{g} \cdot \text{m}^{-3}$)

B.2 Algorithm Development

From the literature review, presented in the previous section, the effects of several physical and chemical factors on chemical and bacteria-assisted pyrite oxidation kinetics were cited. Where available, mathematical relationships

several physical and chemical factors on chemical and bacteria-assisted pyrite oxidation kinetics were cited. Where available, mathematical relationships were also detailed. In this section, algorithms are selected for inclusion in the bacterial kinetics module.

B.2.1 Overall Reaction Rate

The oxidation of pyrite can be expressed by the following expression:

$$\frac{dM}{dt} = -\alpha_p (R_1 + R_2) \quad (B.2.1)$$

where

- M = moles of pyrite per unit volume of tailings ($\text{mol} \cdot \text{m}^{-3}$)
- α_p = surface area of pyrite per unit volume of tailings ($\text{m}^2 \cdot \text{m}^{-3}$)
- R_1 = biological specific rate of reaction ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)
- R_2 = chemical specific rate of reaction ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)

Substituting for α_p with A_p , the total surface area of pyrite (m^2), and V, the volume of tailings (m^3), results in the expression:

$$\frac{dM}{dt} = -\frac{A_p}{V} (R_1 + R_2) \quad (B.2.2)$$

The following sections describe the development of the biological and chemical specific reaction rates.

B.2.2 Biological Rate

The specific rate of reaction employed in the model is that of equation (B.1.4):

$$R_1 = - \frac{\mu x_p}{Y_{x/s}} \quad (B.2.3)$$



where

- X_p = biomass per unit surface area of pyrite (g.m^{-2})
 $Y_{x/s}$ = biomass yield coefficient expressed as g biomass produced per mole of pyrite oxidized (g.mol^{-1})
 μ = specific growth rate of the microbes (mth^{-1})

The principal variables in this relationship are the specific growth rate of the bacteria (μ), the biomass concentration on the pyrite surface (X_p) and the biomass yield coefficient ($Y_{x/s}$). The development of an algorithm for the specific growth rate is outlined below. The biomass yield coefficient and the biomass per unit surface area of pyrite are discussed in detail in Section B.3.

Specific Growth Rate

The specific growth rate in equation (B.2.3) is a function, f , of several variables: temperature, pH, phosphorus concentration, moisture content and carbon dioxide partial pressure.

$$\mu = f[T, \text{pH}, [P], S, P_{\text{CO}_2}] \quad (\text{B.2.4})$$

where

- T = temperature ($^{\circ}\text{K}$)
 P_{CO_2} = partial pressure of carbon dioxide (atm)
 $[P]$ = phosphorus concentration (mol.m^{-3})
 S = degree of saturation; ratio of volumetric water content to porosity ($\text{m}^3.\text{m}^{-3}$)

For the temperature effect, the Arrhenius relationship equation (B.1.9), was employed. The effect of a pH change on the specific growth rate was included using the empirical equation derived from Arkesteyn (1979) data.

The effects of phosphorus concentration and carbon dioxide partial pressure were modelled using Monod type expressions, (see equation (B.1.5)) for each factor and multiplicative kinetics. Multiplicative kinetics assume that the

overall effect of multiple substrate limitation can be modelled by multiplying the effect of one substrate times the other substrate factors. The half saturation constants for the phosphorous and carbon dioxide terms in the equation were modelled with a limiting half-saturation concentration and a limiting half-saturation partial pressure value, respectively.

The effect of moisture contact is modelled using the concept of degree of saturation (S). This is based upon observations by Belly and Brock (1974) and Brock (1975) which showed that bacterial activity increased approximately linearly with increasing water content.

These factors are included in the following multiplicative model employed to predict the specific growth rate:

$$\mu = \mu_{\max} \left(\exp(C_k) \frac{\exp(-E_a/R_g T)}{\text{Temperature}} \underbrace{(1 + 10^{2.5\text{pH}} + 10^{\text{pH}-4.0})^{-1}}_{\text{pH}} \underbrace{\left[\frac{[P]}{L_p + [P]} \right]}_{\text{Phosphorus}} \underbrace{\left[\frac{1.3 P_{\text{CO}_2}}{10^{-4} + P_{\text{CO}_2}} \right]}_{\text{Carbon dioxide}} \underbrace{S}_{\text{moisture}} \right) \quad (\text{B.2.5})$$

where

$\mu_{\max}$ = maximum specific growth rate observed (mth^{-1})

L_p = limiting phosphorus concentration ($\text{mol} \cdot \text{m}^{-1}$)

E_a = activation energy ($\text{cal} \cdot \text{mol}^{-1}$)

R_g = universal gas constant ($\text{cal} \cdot \text{mol}^{-1} \cdot ^\circ\text{K}^{-1}$)

C_k = constant which sets $\mu = \mu_{\max}$ at optimal conditions

The effect of limiting oxygen concentration is not given in the above equation. Rather it is incorporated in the overall pyrite depletion equation presented in Appendix D.

The parameter C_k forces μ to equal $\mu_{\max}$ at standard values of the parameters employed in equation (B.2.5). The parameter C_k is calculated from the following expression:



$$C_k = \ln \left[\exp(E_a/R_g T_{opt}) (1+10^{2.5-pH} + 10^{pH-4.0}) \left(\frac{[P]}{L_p + [P]} \frac{1.3}{10^{-4} + P_{CO2}} \frac{P_{CO2}}{S} \right)^{-1} \right] \quad (B.2.6)$$

The following conditions are considered to be standard:

$$\begin{aligned} pH &= 3.25 \\ T_{opt} &= 303^\circ K \\ E_a &= 11700 \text{ cal.mol}^{-1} \\ R_g &= 1.987 \text{ cal.mol}^{-1}.\text{K}^{-1} \\ [P] &= 2.3 \text{ mol.m}^{-3} \\ L_p &= 1.29 \times 10^{-3} \text{ mol.m}^{-3} \\ P_{CO2} &= 3.2 \times 10^{-4} \text{ atm} \\ S &= 1.0 \text{ m}^3_{\text{w.m}^{-3} \text{ void}} \end{aligned}$$

For these conditions, C_k has a value of 19.737. The standard pH and temperature values are representative of conditions of maximum growth in the study of Arkesteyn (1979). In equation (B.2.4) the upper and lower bounds of pH, 2.5 and 4.0, are the range of optimum growth in the study of Arkesteyn (1979). The Arrhenius activation energy is from Lundgren and Silver (1980).

The limiting phosphorus concentrations of $1.29 \times 10^{-3} \text{ mol.m}^{-3}$ was chosen based on the work of Silver (1986) while the non-limiting phosphorus level used in the model 2.3 mol.m^{-3} , was taken from Hoffmann et al. (1981). The term for carbon dioxide was developed from Hoffmann et al. (1981) data; see Table B.1.1. At a carbon dioxide partial pressure level of $3.2 \times 10^{-4} \text{ atm}$, atmospheric pressure, the Monod expression begins to approach unity.

The value of μ_{max} was estimated using experimental data reported for the specific growth rate, μ , of I. ferrooxidans grown on pyritic material at known temperature and pH conditions. Data from three studies (Arkesteyn, 1980; Hoffmann et al., 1981; Halbert et al., 1983) are available to estimate μ_{max} values. In these studies, an ample supply of phosphorus and oxygen was available for bacterial growth. In addition, the experiments were conducted

under saturated water conditions and at atmospheric carbon dioxide levels. Table B.1.2 presents the data from each study used in the calculation of the respective $\mu_{\max}$ values. The μ values were taken as the slope of the asymptotic region of plots for pyrite depletion versus time. The values of $\mu_{\max}$ were calculated from equation (B.2.5) assuming that a Monod factor of 1 for phosphorus and carbon dioxide, a saturation index of 1, temperature of = 303°K and a pH of 3.25. The average $\mu_{\max}$ values from these studies was 13.0 month⁻¹.

At a temperature of 0°C (273° K) equation (B.2.5) is set equal to zero based on the assumption that microbial activity will cease at this temperature. The freezing point depression caused by salinity has been neglected.

B.2.3 Chemical Rate

The specific rate of chemical oxidation can be represented by the following expression (McKay and Halpern, 1958):

$$R_2 = \frac{-1}{A} \frac{dN_p}{dt} = -r_c f_p P_{O_2} \quad (B.2.7)$$

where

- R_2 = the specific rate of chemical oxidation (mol.m⁻².mth⁻¹)
- N_p = amount of pyrite (mol)
- r_c = chemical rate coefficient (mol.m⁻².mth⁻¹.atm⁻¹)
- P_{O_2} = partial pressure of oxygen (atm)
- A = surface area of pyrite (m²)
- f_p = pH dependence factor (dimensionless)

Employing data from McKay and Halpern (1958) to calculate the chemical rate constant (k_c) results in:

$$r_c = k_c \exp (-E_{ac}/R_g T) \quad (B.2.8)$$



where

- k_c = chemical rate constant; 2.3×10^6 ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1} \cdot \text{atm}^{-1}$)
- R_g = universal gas constant ($1.987 \text{ cal} \cdot \text{mol}^{-1} \cdot ^\circ\text{K}^{-1}$)
- T = absolute temperature ($^\circ\text{K}$)
- E_{ac} = chemical activation energy ($\text{cal} \cdot \text{mol}^{-1}$)

The chemical activation energy employed in the equation (B.2.8) was $13,300 \text{ cal} \cdot \text{mol}^{-1}$. (McKay and Halpern, 1958).

Equation (B.2.8), however, results from experiments carried out at neutral pH conditions, estimated to be at pH 7.0 (McKay, personal communication). To correct for the effect of pH, the chemical rate constant was modified using Smith and Shumate (1970) experimental data to include the pH effect, f_p , as follows:

$$f_p = 0.25 (\text{pH})^{0.70} \quad (\text{B.2.9})$$

This relationship is based upon experimental observations which indicate that $f_p = 1.0$ at $\text{pH} = 7.0$ and $f_p = 0.4$ at $\text{pH} = 2.0$. The power of pH results from interpolation between these points.

B.2.4 Rate of Oxygen Depletion

The rate of oxygen depletion is determined from the stoichiometry of equation (B.1.1) and the pyrite oxidation rate (equation (B.2.1)). It is:

$$R_{O_2} = -3.75 (R_1 + R_2) \frac{\alpha_p}{n_a} \quad (\text{B.2.10})$$

where:

- R_{O_2} = the rate of oxygen depletion ($\text{mol} \cdot \text{m}^{-3} \cdot \text{mth}^{-1}$)
- α_p = surface area of pyrite per unit volume of tailings ($\text{m}^2 \cdot \text{m}^{-3}$)
- n_a = volumetric air content of soil ($\text{m}^3 \cdot \text{m}^{-3}$)

Table B.1.2

CALCULATION OF μ_{MAX} VALUES FROM VARIOUS STUDIES

<u>Study</u>	Parameters			μ_{max} (mth^{-1})
	T (°K)	pH _____	μ mth^{-1} (day^{-1})	
Arkesteyn (1980)	303	3.25	12.9 (0.43)	12.9
Hoffman <u>et al.</u> (1981)	298	3.0	6.6 (0.22±0.2)	13.7
Halbert <u>et al.</u> (1983)	294	2.8	3.5 (0.118)	13.6
	294	2.5	2.7 (0.09)	11.8

Average = 13.0

The surface area from the previous time step is used to estimate α_p . It is anticipated that this procedure produces negligible error.

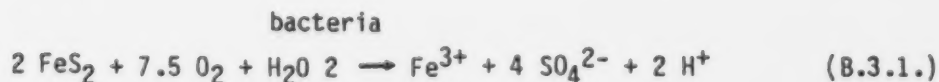
The rate expression in equation (B.2.10) does not include the effect of transport resistances on oxygen for biologically catalized oxidation. But it does for chemical oxidation. The effect of P_{O_2} on the chemical term is removed by making it into a reaction constant analogous to that for the biological term. This results in the chemical term having the form of that of Nicholson (1984). There are some differences because the data of Nicholson suggests a half saturation, partial pressure of .017 atm whereas the value used in this study is 0.01 atm. These differences are negligible, however. The oxygen effects are included in the overall oxygen mass balance presented in Appendix C.

B.3 Parameter Distributions

The following section discusses the nominal values employed for the parameters in the kinetics module, and the associated parameter probability distributions. Table B.3.1 lists the parameters, the probability distribution types and values and the computer source symbols assigned to the parameters.

B.3.1 Biomass Yield Constant

The biomass yield constant ($Y_{x/s}$) is the amount of bacterial protein yielded from the consumption of pyrite. Conventional studies report the yield in terms of protein yield per gram oxygen consumed. The pyrite oxidation stoichiometry can be used to convert units. Numerous investigators (Le Roux, et al., 1973; Lundgren and Silver, 1980; Torma, 1983) have indicated that the oxygen requirement for pyrite oxidation by bacteria is essentially stoichiometric and is given by the following:



This stoichiometry implies that 7.5 moles oxygen is used for every 2 moles pyrite oxidized. Chang and Myerson (1981) reported that the yield is 1.1×10^{-2} to 1.3×10^{-2} grams bacterial protein yield per gram oxygen consumed. This corresponds to 2.2×10^{-2} to 2.6×10^{-2} grams biomass (50% protein content) per gram oxygen consumed.

The range of the biomass yield constant can be estimated as follows:

$$Y_{x/s} = Y_{O_2} \frac{M_{O_2}}{2 \text{ mole FeS}_2} \frac{7.5 \text{ mol O}_2}{2 \text{ mole FeS}_2} \quad (\text{B.3.2.})$$

where $Y_{x/s}$ = biomass yield constant (g biomass mol⁻¹ pyrite)

Y_{O_2} = yield of bacterial protein (g biomass.g⁻¹ oxygen)

M_{O_2} = molecular weight of oxygen (32 g.mol⁻¹)

Using the Myerson (1981) data in the above expression results in a range of 2.64 to 3.12 g biomass per mole FeS₂ for the biomass yield constant.

Arkesteyn (1979) reported his experimental data in terms of moles carbon dioxide (CO₂) fixed per mole pyrite (FeS₂) oxidized. The CO₂ fixation efficiency of chemolithotrophic bacteria is about 67%, i.e. for each mole of carbon fixed, 8 g carbon is incorporated into biomass giving 16 g biomass assuming that (biomass contains 50% carbons). Hence, the biomass yield constant of Arkesteyn's (1979) data was estimated as follows:

$$Y_{x/s} = Y_{CO_2} F_{CO_2} \quad (\text{B.3.3})$$

Y_{CO_2} = mass of bacterial protein yield per mole carbon dioxide consumed (g biomass.mol⁻¹)

F_{CO_2} = moles of CO₂ fixed per mole of pyrite oxidized (mol.mol⁻¹)

The variable F_{CO_2} is a function of the pH. At pH 3.0 F_{CO_2} is equal to 1 mole CO₂ fixed per 5 moles FeS₂ while at pH 4.0 F_{CO_2} is 1 mole CO₂ fixed per 5.6 moles FeS₂ oxidized.

Table B.3.1
KINETICS MODULE PARAMETERS

Model Symbol	Description	Units	Nominal Value	Probability Distribution	Module Source	Computer Symbol
C_k	Kinetic constant	(unitless)	calculated	calculated	Kinetic	CONST
E_a	Biological energy of activation	(cal.mol ⁻¹)	11700	T(10000,11700,16300)	Input	EA1
E_{ac}^{**}	Chemical energy of activation	(cal.mol ⁻¹)	13300	C(13300)	Input	EA2
f_p	pH dependence factor	(unitless)	calculated	calculated	Kinetic	FPH
k_c	Chemical rate constant	(mol.m ⁻² .mth ⁻¹ .atm ⁻¹)	2.3x10 ⁶	T(1.18x10 ⁵ , 2.3x10 ⁶ , 4.72x10 ⁷)	Input	kCONST
L_p	Limiting phosphorus conc.	(mol.m ⁻³)	1.29x10 ⁻³	C(1.29x10 ⁻³)	Input	LP
n_a	Volumetric air content of soil	(m ³ _{air} .m ⁻³ _{tail})	calculated	calculated	Initial	NA(i)
n_t	Porosity	(m ³ _{void} .m ⁻³ _{tail})	0.50	T(0.45,0.50,0.55)	Input	NT
n_w	Water content	(m ³ _{water} .m ⁻³ _{tail})	calculated	calculated	Initial	NW(i)
P_{CO_2}	Partial pressure of carbon dioxide	(%atm)	3.2x10 ⁻⁴	C(3.2x10 ⁻⁴)	Initial	PCO2(i,t)
pH	Measure of hydrogen ion concentration	(unitless)	calculated*	calculated	Speciation	PH(i,t)
R_{O_2}	Rate of oxygen depletion	(mol.m ⁻³ .mth ⁻¹)	calculated	calculated	Kinetic	RO2(i,t)
R_1	Specific rate of biological reaction	(mol.m ⁻² .mth ⁻¹)	calculated	calculated	Kinetic	R1(i,t)
R_2	Specific rate of chemical reaction	(mol.m ⁻² .mth ⁻¹)	calculated	calculated	Kinetic	R2(i,t)
S	Water saturation	(m ³ .m ⁻³)	calculated	calculated	Kinetic	S(i)

Table 8.3.1 cont'd

<u>Model Symbol</u>	<u>Description</u>	<u>Units</u>	<u>Normal Value</u>	<u>Probability Distribution</u>	<u>Module Source</u>	<u>Computer Symbol</u>
μ	Specific growth rate	(mth^{-1})	calculated	calculated	Kinetic	U
μ_{max}	Maximum specific	(mth^{-1})	13.0	U(11.5,14.5)	Kinetics	UMAX
X	Actual depth of layer	(m)	calculated	calculated	Initial	Z
X_p	Biomass per surface area of pyrite	($\text{g}\cdot\text{m}^{-2}$)	1.6×10^{-3}	LN(1.6×10^{-3} , 1.7×10^{-3} , 3.2×10^{-4} , 7.8×10^{-3})	Input	XP
$Y_{x/s}$	Biomass yield coefficient	($\text{g}\cdot\text{mol}^{-1}$)	3.2	T(2.5,3.2,4.2)	Input	YXS
a_p	Surface area per volume of tailings	($\text{m}^2\cdot\text{m}^{-3}$)	calculated*	calculated	Pyrite	ALPHAP(i,t)

NOTE:

- * Calculate during previous time step
- ** Variability of E_{a1} is incorporated in parameter k_c
- m Indicates the months of the year
- i Indicates the particular layer
- t Indicates the overall time period

Key to Probability Distributions:

- C - Constant (Single value)
- LN - Lognormal (geo. mean, geo. std. dev., min., max.)
- N - Normal (mean, std. dev., min., max.)
- T - Triangular (min., mode, max.)
- U - Uniform (min., max.)

Accordingly, Arkesteyn's (1979) data suggests that for a pH of 3.0, the biomass yield constant is 3.2 g biomass produced per mole FeS_2 oxidized. At pH 4.0, the value is 2.86 g biomass produced per mole FeS_2 oxidized.

Beck and Brown (1968) reported their data in terms of moles CO_2 fixed per 100 moles O_2 consumed. Using this data the biomass yield constant can be estimated by:

$$Y_{x/s} = R_f \frac{16 \text{ g cells}}{1 \text{ mole } \text{CO}_2} \frac{7.5 \text{ mol } \text{O}_2}{2 \text{ mol } \text{FeS}_2} \quad (\text{B.3.4})$$

R_f = amount of carbon dioxide fixed per 100 moles of O_2 consumed ($\text{mol} \cdot \text{mol}^{-1}$)

The range of R_f reported by Beck and Brown (1968) was from 5.5 moles CO_2 fixed per 100 moles O_2 consumed to 6.9 moles CO_2 fixed per 100 moles O_2 consumed. This gives a range for the biomass yield from 3.3 to 4.14 g cells per mole FeS_2 oxidized using equation (B.3.4).

Silver and Torma (1974) reported a yield of 0.103 $\mu\text{moles } \text{CO}_2$ fixed per 8.9 $\mu\text{moles } \text{O}_2$ consumed with pyrite as the substrate (pH = 3.5). This converts to an estimated growth yield constant of 0.69 g biomass per mole FeS_2 oxidized using equation (B.3.4).

A summary of the biomass yield constants is presented in Table B.3.2. The overall average value is 2.85 g cells produced per mole of FeS_2 oxidized. For modelling purposes, the lowest value was neglected in computing an average growth yield constant of:

$$Y_{x/s} = 3.2 \frac{\text{g biomass produced}}{\text{mole pyrite oxidized}}$$



B.3.2 Energy of Activation

The energy of activation describes the rate at which a bacterial or chemical reaction changes as a function of temperature. In a study by Halbert et al. (1983), an Arrhenius activation energy of $25.6 \text{ Kcal.mol}^{-1}$ was obtained for bacterial pyrite oxidation, from laboratory experiments carried out at a temperature of 21°C and an initial pH of 3.0. This value implies that the sulphate generation rate increases approximately 5-fold for each 10°C increase in temperature (Halbert et al., 1983).

Lundgren and Silver (1980) determined the energies of activation to be between 11.7 and $16.3 \text{ Kcal.mol}^{-1}$ for ZnS , FeSO_4 , Cu_2S and CuS oxidation.

Halbert et al. (1983) also reported an Arrhenius activation energy of $10.7 \text{ Kcal.mol}^{-1}$ for abiotic pyrite oxidation; a value which corresponds to a doubling of the reaction rate for every 10°C temperature rise. McKay and Halpern (1958) reported an abiotic Arrhenius activation energy of $13.3 \text{ Kcal.mol}^{-1}$.

The Arrhenius activation energies selected for modelling purposes were $11.7 \text{ Kcal.mol}^{-1}$ and $13.3 \text{ Kcal.mol}^{-1}$ for biological and abiological pyrite oxidation, respectively.

B.3.3 Bacterial Population Density

Direct bacterial oxidation of pyrite involves the attachment of bacteria to the mineral surface. Circumstantial evidence for bacterial attachment was first reported by Bryner and Anderson (1957), who observed that weekly drainage of the fluid from the test apparatus did not require reinoculation as ample bacterial population was retained on the solid particles. Since these early studies, bacterial attachment has been confirmed by both microscopic examinations and quantitative evaluations of the adhering biomass (McGoran et al., 1969; Le Roux et al., 1973; Brierley, 1978; Bennett and Tributsch, 1978; Chang and Myerson, 1981; DiSpirito et al., 1982; Myerson and Kline, 1983).

Table B.3.2

BIOMASS YIELD CONSTANTS

Author	Experimental Date given as:	Y _{x/s} Estimate
		(g cells produced/mole FeS ₂ oxidized)
Chang and Myerson (1981)	g protein produced	2.66
	g O ₂ used	3.12
Arkesteyn (1979)	mole CO ₂ fixed	3.20 (pH = 3.0)
	mole FeS ₂ oxidized	2.86 (pH = 4.0)
Beck and Brown (1968)	mole CO ₂ fixed	3.30
	mole FeS ₂ consumed	4.14
Silver and Torma (1974)	mole CO ₂ fixed	0.69 (pH = 3.5)
	mole FeS ₂ consumed	
		Avg. 2.85



The mass of microbes per unit surface area of tailings is the bacterial population density (X_p). The first step in determining X_p is the determination of the number of microbes

$$N_b = \frac{S_c}{A_b} \quad (\text{B.3.5})$$

where

N_b = number of microbes per unit pyrite surface area (number μm^{-2})

S_c = fraction of surface occupied by microbes ($\text{m}^2 \mu\text{m}^{-2}$)

A_b = surface area of microbe (m^2)

The bacterial population density can be calculated from:

$$X_p = N_b V P_b S_b \quad (\text{B.3.6})$$

where

X_p = bacterial mass density ($\text{g} \mu\text{m}^{-2}$)

V = volume of microbes (m^3)

P_b = density of microbes ($\text{g} \mu\text{m}^{-3}$)

S_b = fraction of a microbe that is solid matter

Only a few publications have addressed directly the bacterial coverage of pyritic minerals. Bennett and Tributsch (1978) have shown that bacterial distributions are critically dependent on crystal structure, since bacteria tend to deposit along deviations in the crystal (fracture lines, dislocations where crystal strain energy makes crystal dissolution the favoured location). It follows therefore, that different pyritic crystals will support varying surface population densities. In Bennet and Tributsch's study (1978), scanning electromicrographs showed that pyrite crystals exposed to stationary *I. ferrooxidans* cultures had 3% to 10% surface coverage after 2 years. In all the literature assessed by SENES (1984), the bacterial surface coverage of pyrite ranges from 1% (Chang and Myerson, 1981) to 30% (Le Roux et al., 1973).



In an oxidation study of Denison tailings (SENES, 1983) the bacterial surface coverage was estimated to be 4% in pyritic uranium tailings. This value is within the literature range for pure pyrite grains and suggests that the average is similar for uranium tailings.

The studies described above were made under laboratory conditions. Under field conditions, the surface population density is likely to be less. Silverman (1967) has observed that in-situ tailings contain significantly lower numbers of iron-oxidizing bacteria than tailings used in lysimeter studies.

The surface area of a microbe is estimated to be $6.25 \times 10^{-13} \text{ m}^2$; using a microbe width of $0.5 \text{ }\mu\text{m}$ and length of $1.25 \text{ }\mu\text{m}$ average dimensions (SENES, 1984). Employing the aforementioned bacterial dimensions and surface coverage substitution into equation (B.3.5) results in 1.6×10^{10} to 4.8×10^{11} microbes per m^2 of pyrite surface area.

The volume of the microbe is $2.46 \times 10^{-19} \text{ m}^3$, assuming a cylindrical shape with a radius of $0.25 \text{ }\mu\text{m}$ and length of $1.25 \text{ }\mu\text{m}$. The density of the microbes is about $1 \times 10^6 \text{ g.m}^{-3}$ and the biomass solids content is approximately 20% (Bailey and Ollis, 1977). This gives a range for the bacterial population density of 7.9×10^{-4} to $2.4 \times 10^{-2} \text{ g.m}^{-2}$ (1% to 30% surface coverage).

Thus, the estimated bacterial population density on pyritic surfaces can vary substantially. Furthermore, the bacterial model adapted for this study assumes that the surface density is at steady state. For the purpose of this study a bacterial population density of $4.7 \times 10^{-3} \text{ g.m}^{-2}$ (6% coverage) is used to simulate laboratory conditions and a nominal value of $1.6 \times 10^{-3} \text{ g.m}^{-2}$ (2% coverage) is used to model in-situ tailings oxidation. For the probabilistic trials this parameter is assumed to be log-normally distributed with a mean of $1.6 \times 10^{-3} \text{ g.m}^{-2}$ and a geometric standard deviation of 1.7.

B.3.4 Carbon Dioxide

For tailings layers which are not fully saturated, the partial pressure of carbon dioxide employed in the model is 3.2×10^{-4} atm, the atmospheric carbon dioxide level. For conditions where calcium carbonate is present and active pyrite oxidation occurs, a value of 0.01 atm is employed, based upon field observations of Smyth (1981). This increased value accounts for the CO_2 production during pyrite oxidation and carbonate dissolution.

B.3.5 Chemical Rate Constant

The chemical rate constant, k_c , is an experimentally determined coefficient which is employed in the calculation of the specific rate of chemical oxidation. Employing data from McKay and Halpern (1958) and a chemical activation energy of $13,300 \text{ cal.mol}^{-1}$, a k_c value of $4.72 \times 10^7 \text{ mol.m}^{-2}\text{.mth}^{-1}\text{.atm}^{-1}$ was determined. In order to account for less than optimal conditions in the field as opposed to a laboratory, a triangular distribution was employed with a minimum of $1.18 \times 10^5 \text{ mol.m}^{-2}\text{.mth}^{-1}\text{.atm}^{-1}$, a mode of $2.3 \times 10^6 \text{ mol.m}^{-2}\text{.mth}^{-1}\text{.atm}^{-1}$, and a maximum of $4.72 \times 10^7 \text{ mol.m}^{-2}\text{.mth}^{-1}\text{.atm}^{-1}$.

B.4 Algorithm Calibration/Validation

In the following section the predicted influence of four parameters on the bacterial and chemical rates of pyrite oxidation are compared against experimental data. The parameters examined are water content, pH, temperature and partial pressure of carbon dioxide.

B.4.1 pH

The effect of changes in pH on the rate of biological pyrite oxidation is shown in Figure B.1. The model predicts a maximum rate of pyrite oxidation at pH 3.25. The predicted results closely follow the experimental results of Arkesteyn (1979), Silverman and Lundgren (1959) and Schnaitman *et al.* (1969); the latter two sets of data not being employed in the development of the



model. The degree of agreement with experimental data provides confidence in the pH formulation used in the model.

B.4.2 Temperature

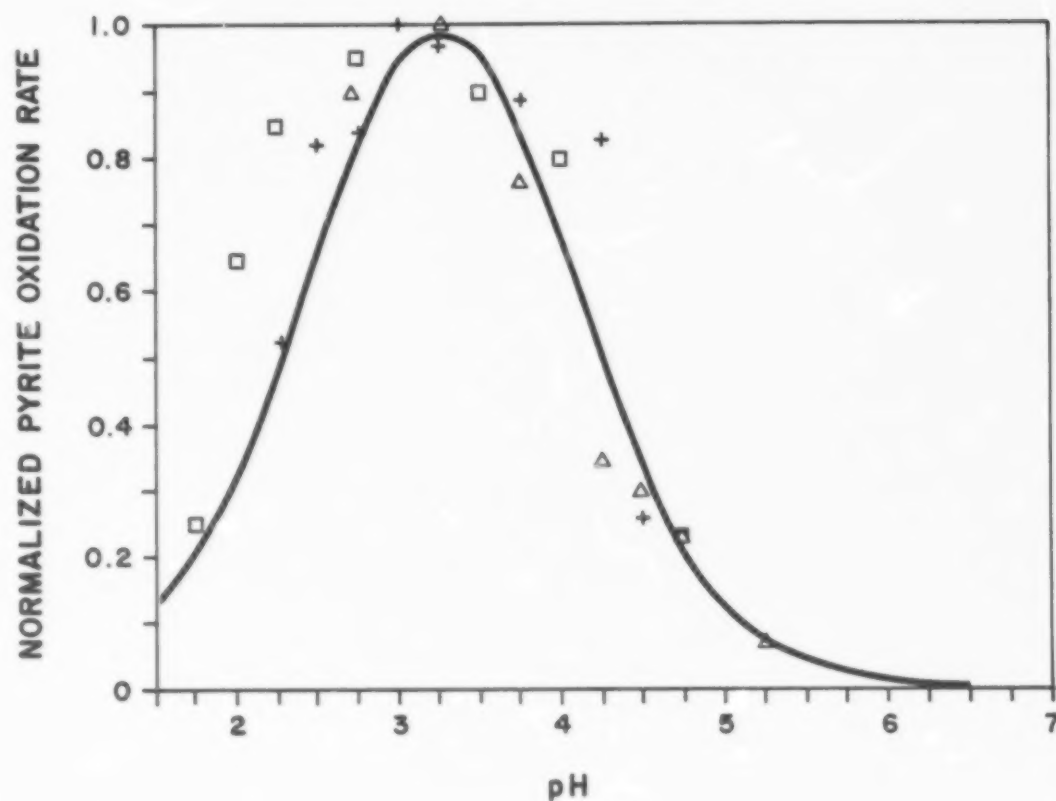
The model predicts an exponential increase in the rate of biological pyrite oxidation with increasing temperature (see Figure B.2). These predictions closely follow the experimental results of Belly and Brock (1974), Malouf and Prater (1961) and Silverman and Lundgren (1959b). In the model it has been assumed that the biological oxidation rate is a maximum at 303°K and a minimum, no oxidation, at 273°K (0°C). The latter temperature does not include the effect of freezing point depression resulting from salinity.

The effect of temperature variations on the chemical rate of pyrite oxidation are shown in Figure B.3. An exponential rate increase is predicted by the model which has no upper or lower boundary conditions on the chemical rate of pyrite oxidation. The predicted results are slightly higher than the experimental data from Cherry et al. (1983).

B.4.3 Carbon Dioxide

The model predicts that the rate of bacterial pyrite oxidation will increase slowly with the partial pressure of carbon dioxide when the latter is greater than 0.08 % atm (see Figure B.4). For carbon dioxide partial pressures less than 0.08 % atm, the model predicts a non-linear and rapid increase in the oxidation rate with increasing partial pressure. The model prediction is similar to the experimental data of Hoffmann et al., (1981) and Torma et al., (1972), but the two data sets show approximately 25% difference in rates. One possible explanation for the difference between the two sets of experimental data is the mineral substrate being oxidized. In the Hoffmann et al., (1981) study, pyrite was being oxidized while in the Torma et al., (1969) work, the substrate was zinc sulfide.

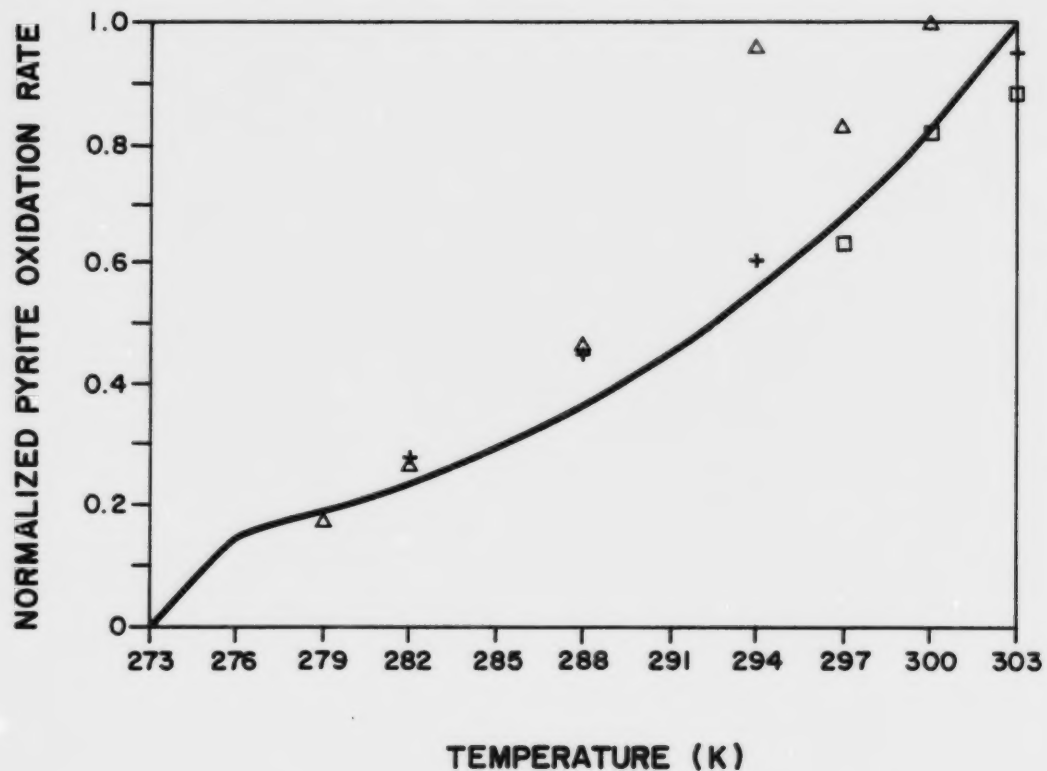
FIGURE B.1
EFFECT OF pH
ON BIOLOGICAL RATE
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS (EQUATION B.2.5)
- + EXPERIMENTAL RESULTS OF SILVERMAN AND LUNDGREN (1959)
- EXPERIMENTAL RESULTS OF SCHNAITMAN *et al* (1967)
- △ EXPERIMENTAL RESULTS OF ARKESTEYN (1979)

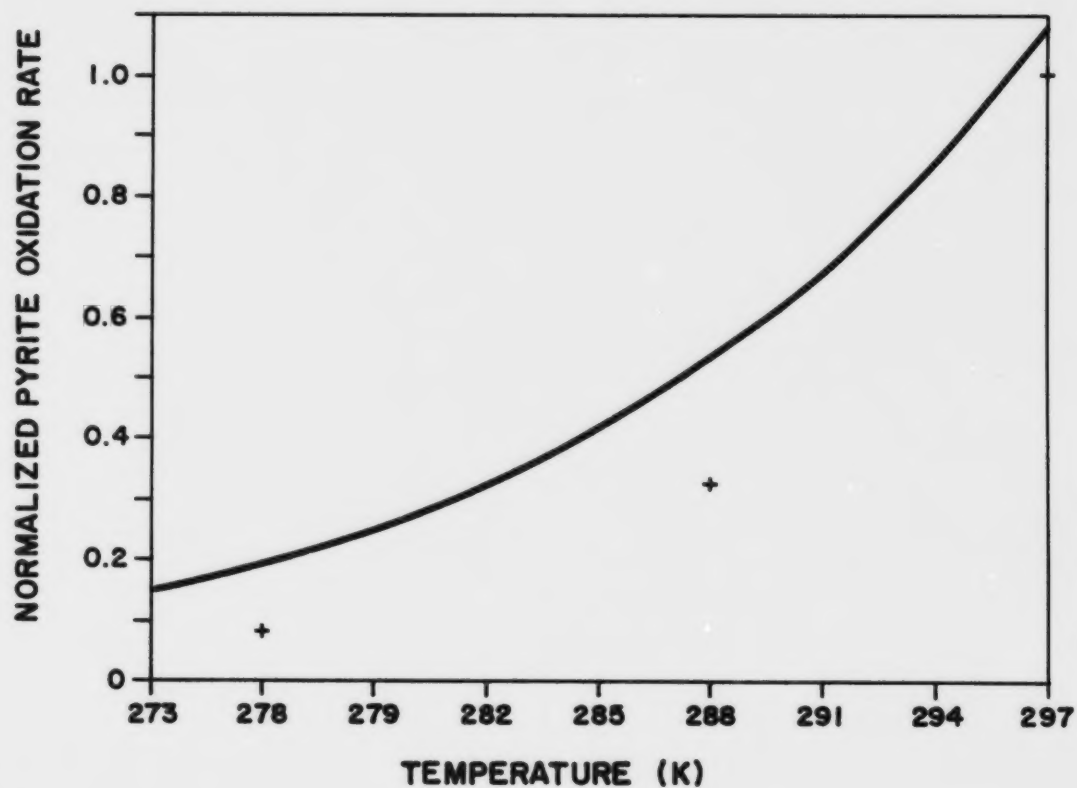
FIGURE B.2
EFFECT OF TEMPERATURE
ON BIOLOGICAL RATE
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS (EQUATION B.2.5)
- + EXPERIMENTAL RESULTS OF MALOUF AND PRATER (1961)
- EXPERIMENTAL RESULTS OF SILVERMAN AND LUNDGREN (1958)
- △ EXPERIMENTAL RESULTS OF BELLY AND BROCK (1974)

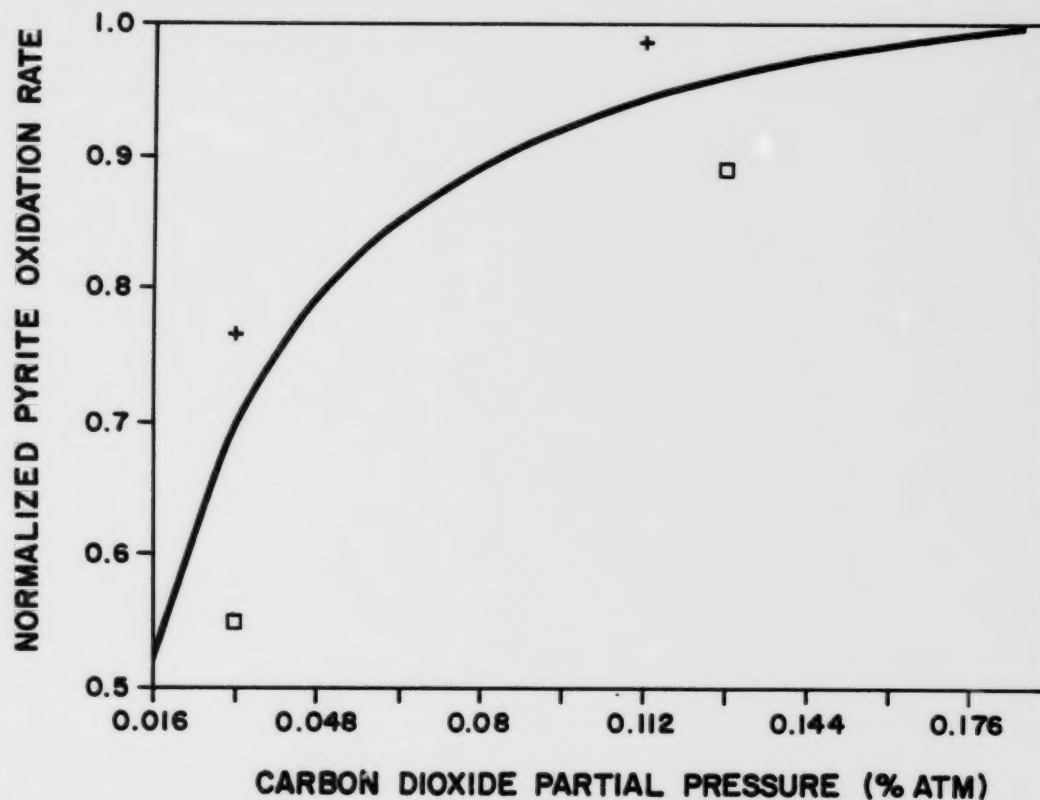
FIGURE B.3
EFFECT OF TEMPERATURE
ON CHEMICAL RATE
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS (EQUATION B.2.10)
+ EXPERIMENTAL RESULTS OF NICHOLSON (1984)

FIGURE B.4
EFFECT OF CARBON DIOXIDE
ON BIOLOGICAL RATE
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF HOFFMAN et al (1981)
- EXPERIMENTAL RESULTS OF TORMA et al (1972)

No data are available on the influence of carbon dioxide partial pressure on the chemical rate of pyrite oxidation. Its effect however, is expected to be minimal.

B.4.4 Water Saturation

A linear relationship between water content and the rate of biological pyrite oxidation is predicted by the model (see Figure B.5). This is consistent with the experiment data of Belly and Brock (1974).

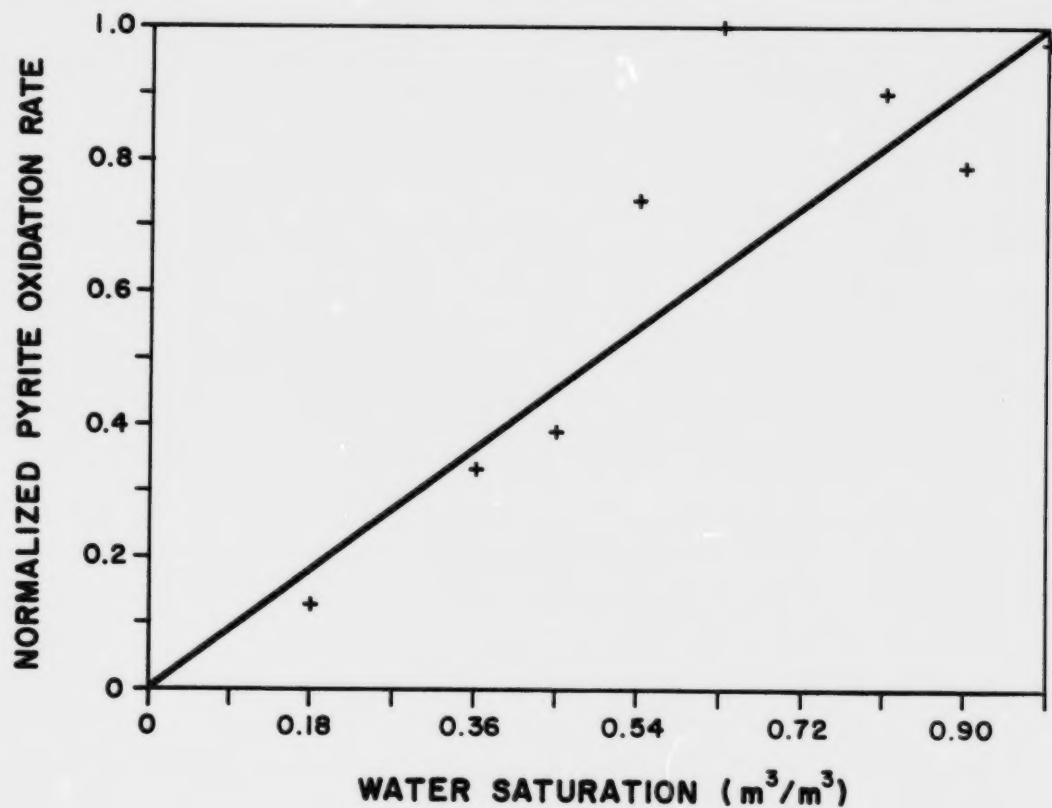
No data are available on the influence of water content on the chemical rate of pyrite oxidation.

B.5 Sensitivity/Uncertainty Analysis

A sensitivity/uncertainty analysis (see chapter 4 for a discussion of the technique used) was performed on the overall Kinetics model. Tables B.5.1 to B.5.2 present sensitivity index results which indicate the influence of the input parameters on the principal calculated model parameters, namely the bacterial rate of pyrite oxidation (R_1) and the chemical rate of pyrite oxidation (R_2). The sensitivity index values, SI, listed on the tables have been limited to the parameters whose SI values exceed 0.1 in each analysis. The analyses were carried out for these depths in the reference tailings pile. (i.e. at 0.2, 1.0 and 2.2m) and at four time intervals (re months 13, 18, 121 and 126).



FIGURE B.5
EFFECT OF WATER SATURATION
ON BIOLOGICAL RATE
(KINETIC MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF BELLY AND BROCK (1974)

Table B.5.1.
Sensitivity Analysis
on the Biological Oxidation Rate

SENSITIVITY OF INPUTS ON R18

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.702E-19	-0.245E-08
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.107E-16	-0.506E-05
2	0.988E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.893E-17	-0.716E-15
3	0.954E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.182E-17	-0.397E-16
4	0.953E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	-0.947E-17	-0.200E-15
5	0.874E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.141E-17	-0.112E-16
6	0.874E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	-0.181E-17	-0.143E-16
7	0.488E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	-0.497E-17	-0.970E-17
8	0.270E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	-0.748E-17	-0.102E-16
9	0.202E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.792E-17	-0.993E-17
10	0.190E+00	-	KCACD3	0.389E-08	0.448E-08	0.513E-08	-0.804E-17	-0.993E-17
11	0.121E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.838E-17	-0.952E-17
12	0.106E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	-0.840E-17	-0.940E-17
LAYER 1 FOR MONTH 18								
1	0.992E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.795E-05	-0.957E-03
1	0.992E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.766E-05	-0.935E-03
2	0.963E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	-0.177E-03	-0.481E-02
3	0.953E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.888E-05	-0.189E-03
4	0.564E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	-0.586E-03	-0.134E-02
5	0.402E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.607E-03	-0.101E-02
6	0.278E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.839E-03	-0.116E-02
7	0.207E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.848E-03	-0.107E-02
8	0.156E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	-0.885E-03	-0.105E-02
LAYER 5 FOR MONTH 18								
1	0.992E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.411E-05	-0.548E-03
2	0.990E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.536E-05	-0.550E-03
3	0.966E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.828E-06	-0.243E-04
4	0.717E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.133E-05	-0.468E-05
5	0.544E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	-0.258E-05	-0.565E-05
6	0.314E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	-0.297E-05	-0.433E-05
7	0.272E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.312E-05	-0.429E-05
8	0.233E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.260E-05	-0.339E-05
9	0.223E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	-0.330E-05	-0.425E-05
10	0.205E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.364E-05	-0.459E-05
11	0.147E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	-0.382E-05	-0.448E-05
12	0.130E+00	-	KCACD3	0.389E-08	0.448E-08	0.513E-08	-0.384E-05	-0.442E-05
13	0.108E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.435E-05	-0.488E-05
14	0.104E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	-0.390E-05	-0.435E-05
15	0.101E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	-0.374E-05	-0.417E-05
LAYER 11 FOR MONTH 18								
1	0.100E+01	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.166E-14	-0.386E-10
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.390E-18	-0.274E-05
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.113E-16	-0.632E-05
1	0.100E+01	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.119E-16	-0.878E-07
2	0.982E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.122E-10	-0.678E-09

SENSITIVITY OF INPUTS ON R18

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
3	0.965E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.173E-10	-0.488E-09
4	0.944E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	-0.936E-11	-0.168E-09
5	0.936E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.155E-10	-0.242E-09
6	0.635E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	-0.177E-10	-0.484E-10
7	0.607E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.174E-10	-0.442E-10
8	0.122E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	-0.415E-10	-0.473E-10

LAYER 11 FOR MONTH 121

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.901E-17
2	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.594E-18	-0.454E-15
3	0.997E+00	-	ICACD3	0.000E+00	0.500E-03	0.100E-02	-0.203E-17	-0.601E-15
4	0.996E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.226E-17	-0.599E-15
5	0.981E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	-0.330E-14	-0.172E-12
6	0.950E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.535E-15	-0.107E-13
7	0.192E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	-0.241E-14	-0.298E-14
8	0.163E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	-0.236E-14	-0.282E-14
9	0.143E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.250E-14	-0.291E-14
9	0.143E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	-0.243E-14	-0.284E-14
10	0.102E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.253E-14	-0.282E-14

LAYER 1 FOR MONTH 126

1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	-0.165E-03
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	-0.303E-03
2	0.524E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	-0.253E-03	-0.531E-03
3	0.509E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.209E-03	-0.425E-03
4	0.501E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	-0.173E-03	-0.347E-03
5	0.343E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.176E-03	-0.267E-03
6	0.168E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.253E-03	-0.304E-03
7	0.130E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	-0.245E-03	-0.282E-03
8	0.125E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.263E-03	-0.301E-03

LAYER 5 FOR MONTH 126

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.238E-03
2	0.923E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.510E-04	-0.665E-03
3	0.746E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.137E-03	-0.540E-03
4	0.736E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	-0.836E-04	-0.317E-03
5	0.636E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	-0.754E-04	-0.207E-03
6	0.630E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	-0.182E-03	-0.490E-03
7	0.453E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	-0.124E-03	-0.227E-03
8	0.367E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.125E-03	-0.198E-03
9	0.206E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	-0.161E-03	-0.203E-03
10	0.167E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	-0.151E-03	-0.182E-03
11	0.165E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.166E-03	-0.199E-03
12	0.142E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	-0.169E-03	-0.197E-03

LAYER 11 FOR MONTH 126

1	0.100E+01	+	EA1	0.100E+05	0.117E+05	0.256E+05	-0.337E-14	-0.171E-07
1	0.100E+01	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.249E-14	-0.193E-10
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.575E-17
1	0.100E+01	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.314E-14	-0.196E-08

SENSITIVITY OF INPUTS ON R18

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
1	0.100E+01	-	KFEEDH	0.127E+01	0.398E+02	0.127E+04	-0.259E-14	-0.195E-09
1	0.100E+01	+	KBAS	0.217E+02	0.227E+02	0.237E+02	-0.683E-14	-0.230E-09
2	0.995E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	-0.277E-14	-0.573E-12
3	0.989E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	-0.251E-14	-0.239E-12
4	0.949E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.575E-15	-0.112E-13
5	0.948E+00	-	XPVR	0.480E-01	0.600E-01	0.720E-01	-0.271E-14	-0.518E-13
6	0.926E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.405E-16	-0.547E-15
7	0.919E+00	-	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.306E-14	-0.380E-13
8	0.879E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	-0.276E-14	-0.227E-13
9	0.847E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	-0.351E-14	-0.229E-13
10	0.817E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.419E-14	-0.229E-13
11	0.803E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	-0.548E-15	-0.278E-14
12	0.781E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.469E-15	-0.214E-14
13	0.744E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	-0.277E-14	-0.108E-13
14	0.735E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	-0.604E-14	-0.228E-13
15	0.716E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	-0.604E-14	-0.213E-13
16	0.586E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	-0.277E-14	-0.670E-14
17	0.548E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	-0.276E-14	-0.612E-14
18	0.543E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	-0.549E-14	-0.120E-13
19	0.530E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	-0.276E-14	-0.587E-14
20	0.510E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	-0.571E-14	-0.116E-13
21	0.116E+00	-	LAM1	0.680E+00	0.730E+00	0.780E+00	-0.561E-14	-0.634E-14



Table B.5.2
Sensitivity Analysis
on the Chemical Oxidation Rate

SENSITIVITY OF INPUTS ON R2

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.996E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.244E-06	-0.638E-04
2	0.534E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.216E-05	-0.463E-05
LAYER 5 FOR MONTH 13								
1	0.981E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.481E-06	-0.258E-04
2	0.792E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.182E-05	-0.872E-05
3	0.499E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.465E-05	-0.928E-05
4	0.105E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.822E-05	-0.918E-05
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.170E-17	-0.191E-10
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.175E-17	-0.109E-04
2	0.953E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	-0.171E-17	-0.361E-16
3	0.840E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.258E-18	-0.161E-17
LAYER 1 FOR MONTH 18								
1	0.998E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.382E-05	-0.156E-02
2	0.400E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.445E-04	-0.742E-04
3	0.106E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.663E-04	-0.741E-04
LAYER 5 FOR MONTH 18								
1	0.996E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.182E-05	-0.409E-03
2	0.580E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.145E-04	-0.346E-04
3	0.519E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.174E-04	-0.361E-04
4	0.405E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.206E-04	-0.346E-04
5	0.132E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.303E-04	-0.349E-04
6	0.128E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.305E-04	-0.350E-04
LAYER 11 FOR MONTH 18								
1	0.100E+01	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.588E-18	-0.602E-11
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.131E-16	-0.338E-07
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.186E-17	-0.103E-04
1	0.100E+01	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.187E-17	-0.139E-07
2	0.981E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.194E-11	-0.104E-09
3	0.944E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	-0.147E-11	-0.261E-10
4	0.935E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.244E-11	-0.376E-10
5	0.663E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	-0.475E-11	-0.141E-10
6	0.617E+00	+	EAI	0.100E+05	0.117E+05	0.256E+05	-0.562E-11	-0.147E-10
7	0.172E+00	-	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.641E-11	-0.774E-11
8	0.170E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	-0.644E-11	-0.775E-11
9	0.158E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	-0.135E-10	-0.160E-10
10	0.118E+00	+	KCACD3	0.389E-08	0.448E-08	0.513E-08	-0.658E-11	-0.747E-11
LAYER 1 FOR MONTH 121								
1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	-0.303E-05
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	-0.194E-06
2	0.562E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.210E-05	-0.480E-05
3	0.346E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.304E-05	-0.465E-05

SENSITIVITY OF INPUTS ON R2

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
2	0.346E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.304E-05	-0.464E-05

LAYER 5 FOR MONTH 121

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.483E-05
2	0.998E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.222E-06	-0.966E-04
3	0.348E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.566E-05	-0.868E-05
4	0.346E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.568E-05	-0.868E-05
5	0.209E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.445E-05	-0.563E-05
6	0.163E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	-0.501E-05	-0.599E-05
7	0.122E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.532E-05	-0.607E-05
8	0.104E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	-0.553E-05	-0.617E-05

LAYER 11 FOR MONTH 121

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.179E-17
2	0.998E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	-0.101E-17	-0.447E-15
2	0.998E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.360E-19	-0.175E-16
3	0.348E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.104E-17	-0.159E-17
4	0.346E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.104E-17	-0.160E-17
5	0.230E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.795E-18	-0.103E-17
6	0.179E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	-0.909E-18	-0.111E-17
7	0.143E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.966E-18	-0.113E-17
8	0.111E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.979E-18	-0.110E-17

LAYER 1 FOR MONTH 126

1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	-0.480E-04
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	-0.390E-05
2	0.445E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	-0.411E-04	-0.740E-04
3	0.354E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.478E-04	-0.740E-04
3	0.354E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.478E-04	-0.740E-04

LAYER 5 FOR MONTH 126

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.174E-04
2	0.996E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.151E-05	-0.420E-03
3	0.355E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.215E-04	-0.333E-04
4	0.354E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	-0.215E-04	-0.333E-04
5	0.184E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.181E-04	-0.222E-04
6	0.114E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	-0.203E-04	-0.229E-04
7	0.111E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.201E-04	-0.226E-04
8	0.109E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	-0.200E-04	-0.225E-04

LAYER 11 FOR MONTH 126

1	0.100E+01	+	EA1	0.100E+05	0.117E+05	0.256E+05	-0.104E-17	-0.373E-10
1	0.100E+01	-	NR1	0.500E-01	0.800E-01	0.110E+00	-0.943E-18	-0.734E-14
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	-0.186E-17
1	0.100E+01	+	V6	0.600E-02	0.300E-01	0.600E-01	-0.119E-17	-0.742E-12
1	0.100E+01	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	-0.953E-18	-0.762E-13
1	0.100E+01	+	KBAS	0.217E+02	0.227E+02	0.237E+02	-0.245E-17	-0.898E-13
2	0.997E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	-0.658E-19	-0.202E-16
3	0.995E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	-0.105E-17	-0.211E-15
4	0.989E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	-0.950E-18	-0.904E-16



SENSITIVITY OF INPUTS ON R2

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
5	0.948E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	-0.102E-17	-0.196E-16
5	0.936E+00	-	UMAX	0.115E+02	0.130E+02	0.145E+02	-0.104E-17	-0.162E-16
7	0.879E+00	+	XALOH	0.140E-02	0.230E-02	0.320E-02	-0.104E-17	-0.860E-17
8	0.859E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	-0.105E-17	-0.744E-17
9	0.847E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	-0.133E-17	-0.867E-17
10	0.811E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	-0.159E-17	-0.840E-17
11	0.744E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	-0.105E-17	-0.409E-17
12	0.727E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	-0.229E-17	-0.838E-17
13	0.708E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	-0.228E-17	-0.782E-17
14	0.586E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	-0.105E-17	-0.253E-17
15	0.548E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	-0.105E-17	-0.232E-17
16	0.534E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	-0.208E-17	-0.445E-17
17	0.521E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	-0.104E-17	-0.218E-17
18	0.496E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	-0.216E-17	-0.428E-17
19	0.354E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	-0.105E-17	-0.163E-17
20	0.241E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	-0.825E-18	-0.109E-17
21	0.116E+00	-	LAM1	0.680E+00	0.730E+00	0.780E+00	-0.212E-17	-0.240E-17

APPENDIX C: OXYGEN TRANSPORT (MODULE III)

C.1 Theoretical Background

C.1.1 Oxygen Transport Processes

There are a number of potential mechanisms contributing to the mass transport of gas through a porous medium. These processes can generally be classified as either diffusive or advective transfer. In the case of oxygen, advective transfer occurs both in the gas phase and as a dissolved constituent in porewater and thus transport can occur in both phases.

Diffusion is the result of random movement of particles due to their kinetic energy. In systems containing gradients in chemical potential (i.e., concentration), however, a mass-flux will be induced. When the oxygen concentration in a surficial porous medium is lower than the atmospheric level, a net diffusive mass flux of oxygen into the deposit results. Diffusion occurs in both the liquid and gas phases; however, because the diffusivity of air is four orders of magnitude greater than that of water, the mass flux in the gas phase should be dominant in a deposit containing interconnecting gas-filled pores. For example, steady state diffusion through gas pores with an effective diffusion coefficient of $10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$ and an oxygen concentration gradient of about $5 \text{ mol} \cdot \text{m}^{-3} \cdot \text{m}^{-1}$ (atmospheric to zero concentration over 2m), would result in an oxygen flux of about $3.67 \text{ mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$.

Advective transfer of oxygen can occur in a number of ways. One important process involves the transport of oxygen dissolved in infiltrating porewater. If the rate of infiltration is known, this component of the oxygen flux can be determined from the equilibrium concentration of dissolved oxygen. This is controlled to some extent by temperature. For example, at 10°C the solubility of atmospheric oxygen in dilute solution is $3.6 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ($3.6 \times 10^{-1} \text{ mol} \cdot \text{m}^{-3}$). If it is assumed that rainfall results in a net infiltration of $0.042 \text{ m} \cdot \text{mth}^{-1}$ ($0.5 \text{ m} \cdot \text{yr}^{-1}$), then the average flux of oxygen would be $0.015 \text{ mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$ or about 250 times lower than the diffusive flux calculated

above.

Other mechanisms for advective transfer include barometric pumping and turbulent flow due to wind action. The relative contribution of these factors, however, is likely to be quite small except for a thin zone at the surface of the sandy to silty tailings. In natural soils that are well-drained, it is expected that most of the gaseous exchange between soil gas and the atmosphere is by gaseous diffusion (Evans, 1965; Kirkham and Powers, 1972). Under other conditions, where pore spaces are almost entirely filled with water (i.e., saturated), the flux of oxygen will be limited by the lower diffusivity in water, as suggested by the results of the calculations comparing the relative magnitudes of diffusive and advective fluxes. Nicholson (1984) found that the infiltration of dissolved oxygen could become an important or dominant component of the downward oxygen flux if diffusion through the pore network is sufficiently restricted by high water content. In either case, separate calculations can be performed to determine the approximate relative importance of each of these mechanisms.

C.1.2 Diffusive Transport

The net transport of mass can be derived from the conditions of continuity in a unit volume (cube) of porous medium. The verbal statement for continuity is:

$$\left(\begin{array}{c} \text{Change of Mass} \\ \text{With Time} \end{array} \right) = \left(\begin{array}{c} \text{Mass Flux} \\ \text{In} \end{array} \right) - \left(\begin{array}{c} \text{Mass Flux} \\ \text{Out} \end{array} \right) + \left(\begin{array}{c} \text{Mass Generated} \\ \text{With Time} \end{array} \right) \quad (\text{C.1.1})$$

Assuming that transport occurs only in one dimension and by diffusion in the gas phase, the resulting relationship can be expressed in terms of concentration of oxygen in the gas phase by:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} + \frac{G}{n_a} \quad (\text{C.1.2})$$

where

D_e = the effective diffusivity through the tailings ($m^2.mth^{-1}$)

t = time (mth)

X = the depth below the surface (m)

G = the reaction term ($mol.m^{-3}.mth^{-1}$)

n_a = the volumetric gas content ($m^3_{air}.m^{-3}_{tail}$)

C = air phase oxygen concentration ($mol.m^{-3}$)

An approximate rate equation for pyrite oxidation is adapted to replace G in the above equation. The empirical relationship can be expressed for a first-order reaction and for a zero-order reaction as:

$$\frac{-dC}{dt} = K_b C \quad (C.1.3a)$$

and;

$$\frac{-dC}{dt} = R \quad (C.1.3b)$$

where

K_b = the temperature dependent first-order rate constant (mth^{-1})

R = zero-order rate constant ($mol.m^{-3}.mth^{-1}$)

The parameter K_b in turn is calculated from:

$$K_b = \frac{R}{K_m} \quad (C.1.4)$$

where

K_m = the half saturation constant ($mol.m^{-3}$)



Based on a unit volume of porous medium the first-and zero-order relationships become:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{K_b C}{n_a} \quad (C.1.5a)$$

and

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{R}{n_a} \quad (C.1.5b)$$

It has been shown that the transient equations can be reduced to steady state when conditions are appropriate. The time to attain steady state has been shown to be a function of the ratio of the reaction rate constant to the effective diffusivity (K_b/D_e or R/D_e). In relative terms when K_b/D_e is large, the time to attain steady state is small (Nicholson, 1984). When oxidation rates are greater than or equal to those expected for chemical oxidation of pyrite at neutral pH in tailings even with low pyrite contents (i.e., low K_b value), steady state conditions will probably be attained before one month's time. When pyrite oxidation rates are higher such as when bacteria are involved or when the pyrite content is higher, steady-state will be attained in a much shorter time. When steady state conditions apply, the controlling equations reduce to:

$$D_e \frac{\partial^2 C}{\partial x^2} - K_b C = 0 \quad (C.1.6a)$$

and

$$D_e \frac{\partial^2 C}{\partial x^2} - R = 0 \quad (C.1.6b)$$

C.1.3 Advective Transport

The advective transport of oxygen, described here, is limited to movement of dissolved oxygen with the downward moving porewater. In this case the reaction term is the same as in equation (C1.6a) above but the flux term is replaced by the advective component as:

$$V \frac{\partial C_w}{\partial x} - \frac{K_b C_w}{n_w} = 0 \quad (C.1.7)$$

where

V = the velocity of the porewater (m.mth⁻¹)

C_w = the aqueous concentration of oxygen (mol.m⁻³)

n_w = the volumetric soil water content (m³_{air}.m⁻³_{tail})

This mechanism is significant when the diffusive flux of oxygen is restricted to levels that are controlled by diffusion through water in contrast to diffusion through the gas phase that can be four orders of magnitude greater. In fact there is a continuum of contribution between diffusion and advection in which one or the other mechanism dominates at extremes and the mechanisms are additive in the transition range of values. Here they are treated as separate mechanisms but because the transition range is expected to be small, little error should result from this approximation. Because the movement of water and the dissolved saturated oxygen concentration are relatively constant, the advective flux term will be relatively constant. Therefore the transition of diffusive flux to advective is based almost entirely on the change in effective diffusivity of the tailings. In the low range of diffusivities, Reardon and Moddle (1985) show that the slope of $(\log D_e)/n_a$ is quite large. This means that at the water table or more precisely at the top of the capillary fringe, the value of D_e will change abruptly by orders of magnitude resulting in the change in importance from diffusive control to advective control.

C.2 Algorithm Development

C.2.1 Modelling Approach

Oxygen transport into the tailings mass is driven by both gradients in concentration that result in diffusion and the flow of infiltrating water that contains dissolved oxygen. In a homogeneous medium, the solution to this problem is relatively simple and an exact solution is available. Such



representation is not reasonable for tailings, however, because many properties are depth dependent or at least are variable, often in a layered fashion. It is preferable, therefore, to solve the problem with the capability to handle parameter variation (i.e., K_b , D_e) with depth. This can be accomplished by numerical approximation to the controlling equation. However, it is preferable to develop an exact solution where the solution is most crucial, that is in the regions of steep oxygen gradients. At depths near the water table, the lower concentrations result in less sensitivity to the problem of determining oxidation rates and hence an approximation there is not likely to be problematic.

The model developed here is based on discretization of the tailings into "layers" that are homogeneous within each layer but the properties of each layer can vary. The problem remains one dimensional in that flux occurs only in the downward direction with respect to oxygen. An appropriate solution is therefore applied to the series of stacked layers between which the concentrations and fluxes are coupled.

C.2.2 Analytical Solutions

Unsaturated Zone

i) Diffusion Case

The nature of the problem requires the solution to oxygen concentrations over discrete intervals of tailings. One way to solve this is to apply an exact (analytical) solution to each layer, and then to couple the layers through the appropriate boundary conditions. For the first-order reaction at steady state, the exact solution for flux across any interval where concentrations are known at the boundaries is given as (Carslaw and Jaeger, 1959):

$$F_t = D_e (UC_1 \cosh (U dx) - UC_2) / \sinh (U dx) \quad (C.2.1)$$

and

$$F_b = D_e (UC_1 - UC_2 \cosh (U dX)) / \sinh (U dX) \quad (C.2.2)$$

where

- F_t = flux at the top of the boundary layer ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)
- F_b = flux at the bottom of the boundary layer ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)
- C_1 = the oxygen concentration in the upper boundary layer ($\text{mol} \cdot \text{m}^{-3}$)
- C_2 = the oxygen concentration in the lower boundary layer ($\text{mol} \cdot \text{m}^{-3}$)
- U = square root of the ratio of the reaction rate constant (bulk) to the effective diffusivity of the layer $(K_b/D_e)^{0.5}$ (m^{-1})
- dX = thickness of a layer (m)
- D_e = effective diffusivity through the tailings ($\text{m}^2 \cdot \text{mth}^{-1}$)
- K_b = bulk reaction rate constant (mth^{-1})

Linking the fluxes at adjoining layers gives the general equation in terms of concentration at three successive interfaces as:

$$\begin{aligned} & (D_i U_i / \sinh (U_i dX_i)) C_{i-1} \\ & - ((D_i U_i / \tanh(U_i dX_i)) \\ & + (U_{i+1} D_{i+1} / \tanh(U_{i+1} dX_{i+1}))) C_i \\ & + (U_{i+1} D_{i+1} / \sinh (U_{i+1} dX_{i+1})) C_{i+1} = 0 \end{aligned} \quad (C.2.3)$$

where

- D_i = the effective diffusivity of layer i ($\text{m}^2 \cdot \text{mth}^{-1}$)
- C_i = oxygen concentration at the lower boundary ($\text{mol} \cdot \text{m}^{-3}$)
- C_{i-1} = oxygen concentration at the upper boundary ($\text{mol} \cdot \text{m}^{-3}$)
- C_{i+1} = oxygen concentration at the bottom boundary ($\text{mol} \cdot \text{m}^{-3}$)
- U_i = square root of the ratio of the reaction rate constant to the effective diffusivity of layer i (K_b/D_i) (m^{-1})
- dX_i = thickness of layer i (m)

The zero-order solution is also developed by linking the fluxes across the layer interfaces where the fluxes are determined as:



$$F_t = R \, dX/2 + D_e C_1/dX - D_e C_2/dX \quad (C.2.4)$$

and

$$F_b = -R \, dX/2 + D_e C_1/dX - D_e C_2/dX$$

Linking the adjoining layers and solving for C gives the following expression:

$$R_i \, dX_i/2 + R_{i+1} \, dX_{i+1}/2 = (D_i/dX_i)C_{i-1} - ((D_i/dX_i) + (D_{i+1}/dX_{i+1}))C_i + (D_{i+1}/dX_{i+1})C_{i+1} \quad (C.2.5)$$

where the notation is the same as that given for the first-order case.

When pyrite (sulphide mineral) is not present, the diffusive flux is simply expressed by Fick's first law:

$$F = D_i \, (C_i - C_{i-1}) / dX_i \quad (C.2.6)$$

where

$$F = \text{the flux of oxygen across the top boundary (mol.m}^{-2}\text{.mth}^{-1}\text{)}$$

Linking the diffusive fluxes at adjoining layers gives the following general equation:

$$(D_i/dX_i)C_{i-1} - ((D_i/dX_i) + (D_{i+1}/dX_{i+1}))C_i + (D_{i+1}/dX_{i+1})C_{i+1} = 0 \quad (C.2.7)$$

ii) Advection Case

When the diffusivity is small, the flux of dissolved oxygen being transported by infiltrating water will be greater than the diffusive flux. The advective flux is trivial but provides a boundary condition at the top of the capillary fringe and can be expressed as:

$$F = V \, C_{wb} \, K_H \quad (C.2.8)$$

where

C_{wb} = the concentration of oxygen (in solution) at the boundary ($\text{mol} \cdot \text{m}^{-3}$)

V = the rate of infiltration of water ($\text{m} \cdot \text{mth}^{-1}$)

K_H = Henry's Law Constant ($\text{m}^3 \cdot \text{m}^{-3}$)

Saturated Zone

Once the oxygen concentration has been calculated for the top layer of the capillary fringe, the following infiltration equation can be employed to determine the oxygen profile in the saturated zone:

$$C_{wi} = C_{wb} \cdot \exp(-K_b \cdot X/V) \quad (\text{C.2.9})$$

where

C_{wi} = the concentration of oxygen (in solution) in layer i ($\text{mol} \cdot \text{m}^{-3}$)

X = distance between the boundary and the midpoint of layer i (m)

C.2.3 Boundary Conditions

The solution to the concentration problem requires that boundary conditions be applied. The condition for the top boundary is trivial because atmospheric oxygen is present at the surface of the tailings meaning that the concentration is fixed for all time. The condition at the bottom of the tailings requires that the flux be constant and equal to $C_w V$.

In practical terms, these boundaries must be applied for the cases where first-order, zero-order and no-reaction conditions apply. Therefore, there are three general cases for the upper boundary and three cases for the bottom boundary.

The zero-order reaction applies when oxygen occurs above a certain minimum concentration and the process converts to first-order when the oxygen content

falls below this value. This means that it is possible to have zero-order (above) to first-order interfaces through the column of tailings layers. Similarly, it is possible to develop a condition of no-reaction (above - due to pyrite depletion) to first- or zero-order reaction (below) at specific depths in the profile. All of these conditions must be formulated and solved. In all, there are 6 specific equations that apply to the top boundary, 6 equations for the intermediate layers and 3 equations for the bottom boundary.

An additional boundary condition for seasonal freezing of the ground surface has been applied to the top layer. When the soil temperature is equal to or less than 0°C (273°K) the effective diffusivity is calculated using an air content of $0.10 \text{ m}^3.\text{m}^{-3}$. This was done in an attempt to simulate the freezing of the top layer. The net result of this substitution is a decrease in the oxygen flux across the top layer during the winter months.

C.2.4 Overall Solution

Oxygen transport and oxygen consumption are described by coupling the various solutions at the appropriate boundaries. When pyrite is present throughout the tailings profile, for instance, and the oxygen concentration is below a specified value, diffusive transport dominates and equation (C.2.3) applies for layers where gas-filled pores are present. The equations are coupled at the interface between the two regimes. When the pyrite has been depleted in any layer or is not present for whatever reason, the controlling equations change.

The general equation that applies to all conditions is a linear algebra problem of the form:

$$\underline{A} \underline{C} = \underline{W} \quad (\text{C.2.9})$$

where

- $\underline{A}$ = the matrix of coefficients (m.mth^{-1})
- $\underline{C}$ = the concentration of oxygen with depth ($\text{mol}.\text{m}^{-3}$)
- $\underline{W}$ = the loading term ($\text{mol}.\text{m}^{-2}.\text{mth}^{-1}$)

There are three A and one W coefficients for each specific condition. Only the values of the coefficients change among the 15 different conditions possible. The A and W coefficients and the controlling conditions are listed in Table C.2.1. The matrix that results from these equations for the sequence of layers is tridiagonal with the dominant diagonal containing the A coefficients for the middle interface and the upper and lower diagonals containing the upper and lower interface coefficients respectively. The mathematical solution is found by simultaneous solution of the N equations where N equals the number of interfaces or layers. In this way, the resulting concentration in each layer is based on the exact mathematical solution for the tailings profile system.

C.3 Parameter Distributions

The oxygen transport model requires parameters for each layer that includes the effective diffusion coefficient (D_e) and the rate constant (K_b or R). The porewater velocity (V) is required at the water table. The other parameters are imposed in the model and the values are selected to provide model sensitivity and to minimize numerical error in subsequent mass balance and mass transfer calculations. The rate constants are calculated in a separate module in the program and are based on the values of other parameters.

Table C.3.1 lists the probability distribution types and descriptions and the computer source symbols assigned to the parameters.

C.3.1 Effective Diffusivity

To calculate the effective diffusivity (D_e) of the tailings the following expression, experimentally determined from tailings at Elliot Lake, was employed (Reardon and Moddle 1985):

$$D_e = 52.56 \left(\frac{n_a - 0.05}{0.95} \right)^{1.7} \quad (C.3.1)$$

where

n_a = volumetric air content of the soil ($\text{m}^3_{\text{air}} \cdot \text{m}^{-3}_{\text{tail}}$)

D_e = effective diffusivity of oxygen ($\text{m}^2 \cdot \text{mth}^{-1}$)

The above expression has a lower limit of $0.05 \text{ m}^3 \cdot \text{m}^{-3}$ for n_a . When the temperature in the top layer is equal to or less than 0°C (273°K), n_a is set equal to the $0.10 \text{ m}^3 \cdot \text{m}^{-3}$.

Figure C.1 presents the data from which the empirical relation given in equation C.3.1 was derived.

C.3.2 Infiltration Rate

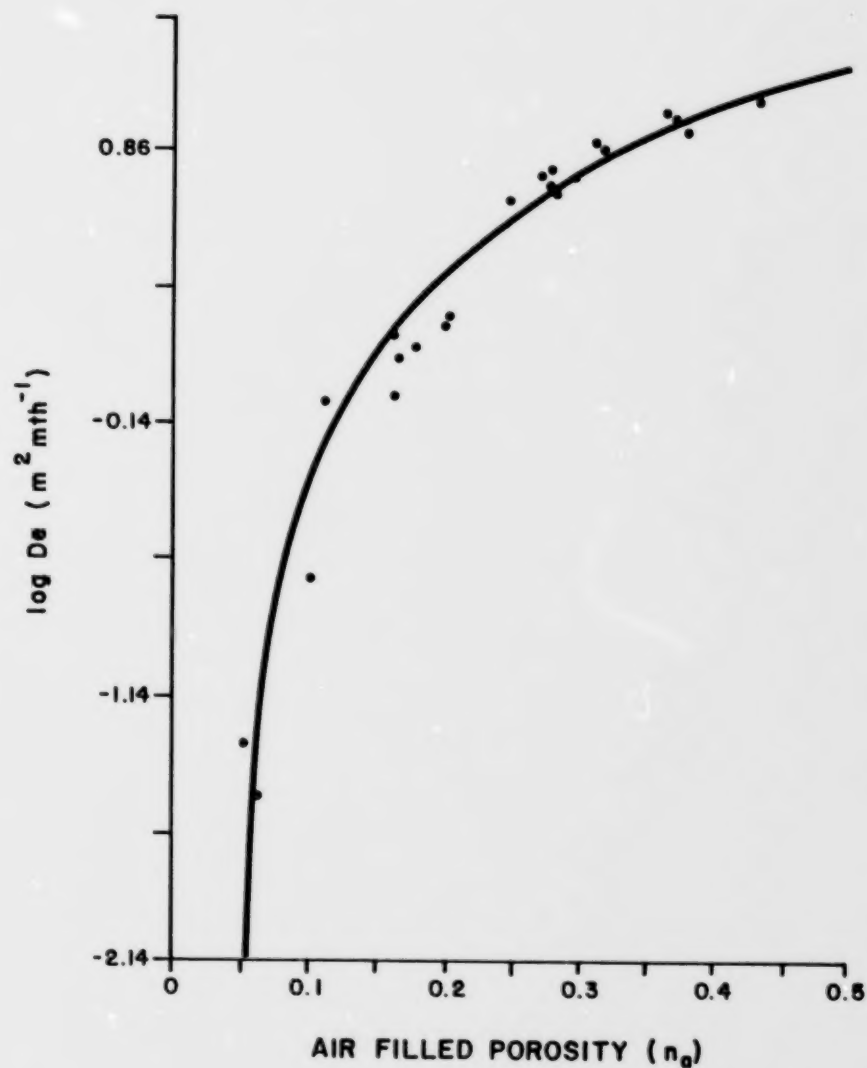
The infiltration rate is the velocity of the porewater (V). The actual parameter values employed and a more detailed description of the parameter are presented in Appendix F.

C.4 Algorithm Calibration/Validation

To validate the performance of the oxygen transport module, model predictions were compared to field data. Oxygen profile measurements reported by Golder Associates (1981) for the Stanrock tailings area in Elliot Lake were used for this purpose. The monitoring was performed on 18 November 1981. The Stanrock tailings are a sandy type of tailings with a high microbial activity. The water table depths, Z , at the piezometer nests used in determining the oxygen profile were 3.2 m, (10.5 ft) at PN-8, and 1.2 m (4 ft) at PN-3.

The soil temperature, effective diffusivity, water content, pH and rate of pyrite oxidation were all calculated by the model. The majority of the parameter values employed in the calculation of the aforementioned variables are the nominal values presented for each module. The site specific data used is presented in Table C.4.1. The selected value for the bacterial population density, X_p , represents its upper limit.

FIGURE C.1
EXPERIMENTALLY DETERMINED
AND CALCULATED VALUES OF EFFECTIVE DIFFUSIVITY



SOURCE: REARDON AND MODELLE (1985)

continued Table C.2.1

Middle Layers Where $I = 2$ to N

Case II.1: Zero Order - Zero Order

$$A_{i,1} = D_i/dX_i$$

$$A_{i,2} = - (D_i/dX_i + D_{i+1}/dX_{i+1})$$

$$A_{i,3} = D_{i+1}/dX_{i+1}$$

$$W_i = R_i dX_i/2 + R_{i+1} dX_{i+1}/2$$

Case II.2: First Order - First Order

$$A_{i,1} = D_i U_i / \sinh (U_i dX_i)$$

$$A_{i,2} = - \left(\frac{U_i D_i \cosh (U_i dX_i) / \sinh (U_i dX_i) + U_{i+1} D_{i+1} \cosh (U_{i+1} dX_{i+1}) / \sinh (U_{i+1} dX_{i+1})}{\cosh (U_{i+1} dX_{i+1}) / \sinh (U_{i+1} dX_{i+1})} \right)$$

$$A_{i,3} = U_{i+1} D_{i+1} / \sinh (U_{i+1} dX_{i+1})$$

$$W_i = 0$$

Case II.3: No pyrite - No pyrite

$$A_{i,1} = D_i/dX_i$$

$$A_{i,2} = - (D_i/dX_i + D_{i+1}/dX_{i+1})$$

$$A_{i,3} = D_{i+1}/dX_{i+1}$$

$$W_i = 0$$

continued Table C.2.1

Case II.4: No pyrite - Zero Order

$$A_{i,1} = D_i/dX_i$$

$$A_{i,2} = - (D_i/dX_i + D_{i+1}/dX_{i+1})$$

$$A_{i,3} = D_{i+1}/dX_{i+1}$$

$$W_i = R_{i+1}dX_{i+1}/2$$

Case II.5: No pyrite - First Order

$$A_{i,1} = D_i/dX_i$$

$$A_{i,2} = - (D_i/dX_i + D_{i+1}U_{i+1} \cosh (U_{i+1} dX_{i+1})/\sinh (U_{i+1} dX_{i+1}))$$

$$A_{i,3} = D_{i+1}U_{i+1}/\sinh (U_{i+1} dX_{i+1})$$

$$W_i = 0$$

Case II.6: Zero Order - First Order

$$A_{i,1} = D_i/dX_i$$

$$A_{i,2} = - (D_i/dX_i + D_{i+1}U_{i+1} \cosh (U_{i+1} dX_{i+1})/\sinh (U_{i+1} dX_{i+1}))$$

$$A_{i,3} = D_{i+1}U_{i+1}/\sinh (U_{i+1} dX_{i+1})$$

$$W_i = + R_i dX_i/2$$

continued Table C.2.1

Bottom Boundary Where $I = N$

Case III.1: Zero Order - Advective

$$A_{N1} = D_N/dx_N$$

$$A_{N2} = - (D_N dx_N + K_H V)$$

$$A_{N3} = 0$$

$$W_N = + R_N L_N/2$$

Case III.2: First Order - Advective

$$A_{N1} = D_n U_N/\sinh (U_N dx_N)$$

$$A_{N2} = - (U_N D_N \cosh (U_N dx_N)/\sinh (U_N dx_N) + K_H)$$

$$A_{N3} = 0$$

$$W_N = 0$$

Case III.3: No pyrite - Advective

$$A_{N1} = D_N/L_N$$

$$A_{N2} = - (D_N/dx_N + K_H)$$

$$A_{N3} = 0$$

$$W_N = 0$$

continued Table C.2.1

Case I.4: No pyrite - Zero Order

$$A_{11} = 0$$

$$A_{12} = - (D_1/dX_1 + D_2/dX_2)$$

$$A_{13} = D_2/dX_2$$

$$W_1 = R_2 dX_2/2 - D_1 C_0/dX_1$$

Case I.5: No pyrite - First Order

$$A_{11} = 0$$

$$A_{12} = - (D_1/dX_1 + D_2 U_2 \cosh (U_2 dX_2)/\sinh (U_2 dX_2))$$

$$A_{13} = U_2 D_2/\sinh (U_2 dX_2)$$

$$W_1 = - D_1 C_0/dX_1$$

Case I.6: Zero Order - First Order

$$A_{11} = 0$$

$$A_{12} = (- D_1/dX_1 + D_2 U_2 \cosh (U_2 dX_2)/\sinh (U_2 dX_2))$$

$$A_{13} = U_2 D_2/\sinh (U_2 dX_2)$$

$$W_1 = - R_1 dX_1/2 - D_1 C_0/dX_1$$

Table C.3.1

OXYGEN TRANSPORT MODULE PARAMETERS

Model Symbol	Description	Units	Nominal Value	Probability Distribution	Module Source	Computer Symbol
C_0	initial oxygen concentration in air phase at surface	(mol.m ⁻³)	calculated	calculated	Oxygen	CO
C	oxygen concentration in air phase	(mol.m ⁻³)	calculated	calculated	Oxygen	COX(i,t); C(i)
C_w	oxygen concentration in porewater	(mol.m ⁻³)	calculated	calculated	Oxygen	CW(i)
D_e	effective diffusivity through tailings	(m ² .mth ⁻¹)	calculated	calculated	Oxygen	DE(i)
dX	thickness of each layer	(m)	0.20	C(0.20)	Input	DX(i)
h	height above water table	(m)	calculated	calculated	Oxygen	H(i)
K_m	half saturation constant	(mol.m ⁻³)	calculated	calculated	Oxygen	KHALF
K_b	bulk oxygen reaction rate constant	(mth ⁻¹)	calculated	calculated	Oxygen	KB(i)
L	number of layers	(unitless)	22	C(22)	Input	L
L_s	layers to saturated zone	(unitless)	21	C(21)	Input	LS
U	ratio of oxygen reaction rate to diffusivity	(m ⁻¹)	calculated	calculated	Oxygen	UR(i)
n_a	volumetric air content of soil	(m ³ .m ⁻³)	calculated	calculated	Kinetic	NA(i)
n_w	calculated water content of tailings	(m ³ water.m ⁻³ tail)	calculated	calculated	Initial	NW(i)
n_r	residual water content	(m ³ water.m ⁻³ tail)	0.08	N(0.08,0.01,0.05,0.11)	Input	NR
n_t	porosity	(m ³ void.m ⁻³ tail)	0.5	T(0.45,0.5,0.55)	Input	NT(i)
K_H	Henry's Law constant for oxygen	L.m ⁻³	23.6	C(23.6)	Input	HENRY
R	rate of oxygen depletion	(mol.m ⁻³ .mth ⁻¹)	calculated	calculated	Kinetic	RO2(k,t);R(i)
V	infiltration rate of water into tailings	(m.mth ⁻¹)	calculated	calculated	Input	VRAIN(m)
Z	depth to water table	(m)	3.0	C(3.0)	Input	ZWATER
λ	soil coefficient	(unitless)	0.78	U(0.68,0.78)	Input	LAM

NOTE:

- m Indicates the months of the year.
i Indicates the particular layer.
t Indicates the overall time period.

Key to Probability Distributions:

- C - Constant (single value)
N - Normal (mean, std. dev., min., max.)
T - Triangular (min., mode, max.)
U - Uniform (min., max.)

Table C.4.1 .

PARAMETER VALUES EMPLOYED IN THE PREDICTION OF THE OXYGEN PROFILE

<u>Parameter</u>	<u>Units</u>	<u>Value</u>
x_p	(g.m ⁻²)	7.8×10^{-3}
n_r	(m ³ .m ⁻³)	0.04
n_t	(m ³ .m ⁻³)	0.40
h_e	(m)	0.1
λ	(unitless)	0.68
dX	(m)	0.15
L	(unitless)	20
Z (PN-8)	(m)	3.2
Z (PN-3)	(m)	1.2

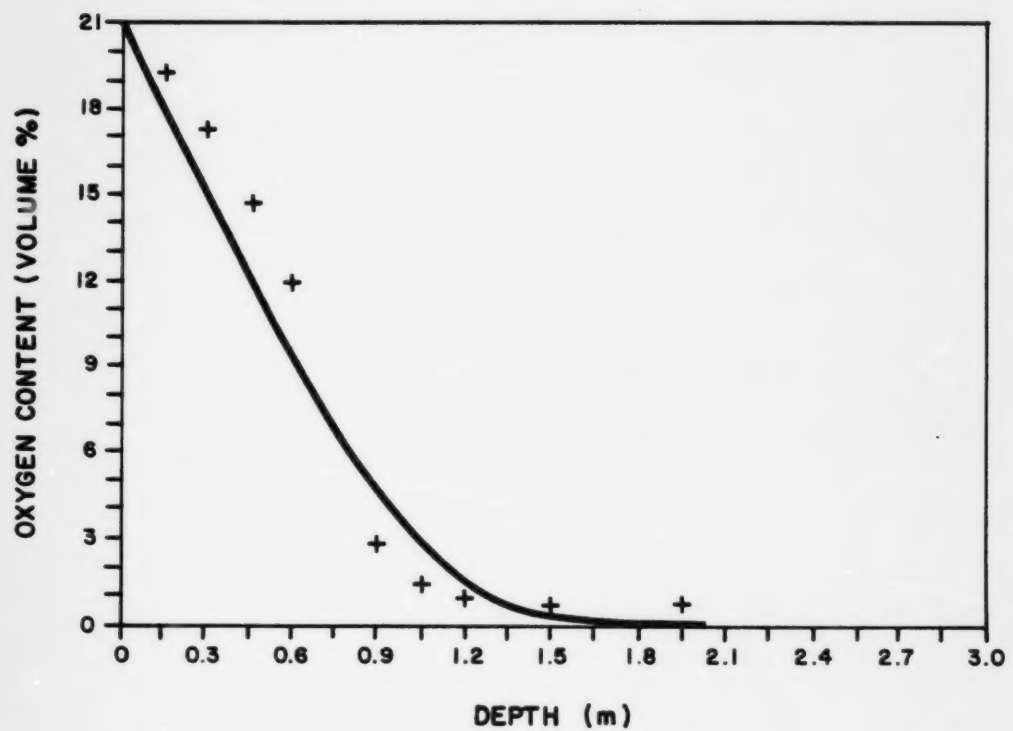
The measured field data and the model's predicted oxygen profiles are presented on Figures C.2 and C.3. The predicted oxygen profile closely resembles the observed values for the deep water table case, Figure C.2. Both model and field data predict limiting oxygen concentrations at approximately 1.5 m.

In Figure C.3, the model's predictions are compared against field data for a site with a shallow water table. In this case the model under predicts the large decrease in oxygen concentration between the 0.4 m and 0.8 m depths. The overall trends however, are similar.

C.5 Sensitivity/Uncertainty Analysis

A sensitivity/uncertainty analysis was performed on the oxygen transport model. Table C.5.1 summarizes the results of the sensitivity index technique discussed in chapter 4 which measures the influence of model input parameters on the partial pressure of oxygen. The sensitivity analysis was carried out for three depths in the tailings mass and for four time periods, as discussed previously in Appendix B. Only the parameters with sensitivity index values, SI, greater than 0.1 are presented.

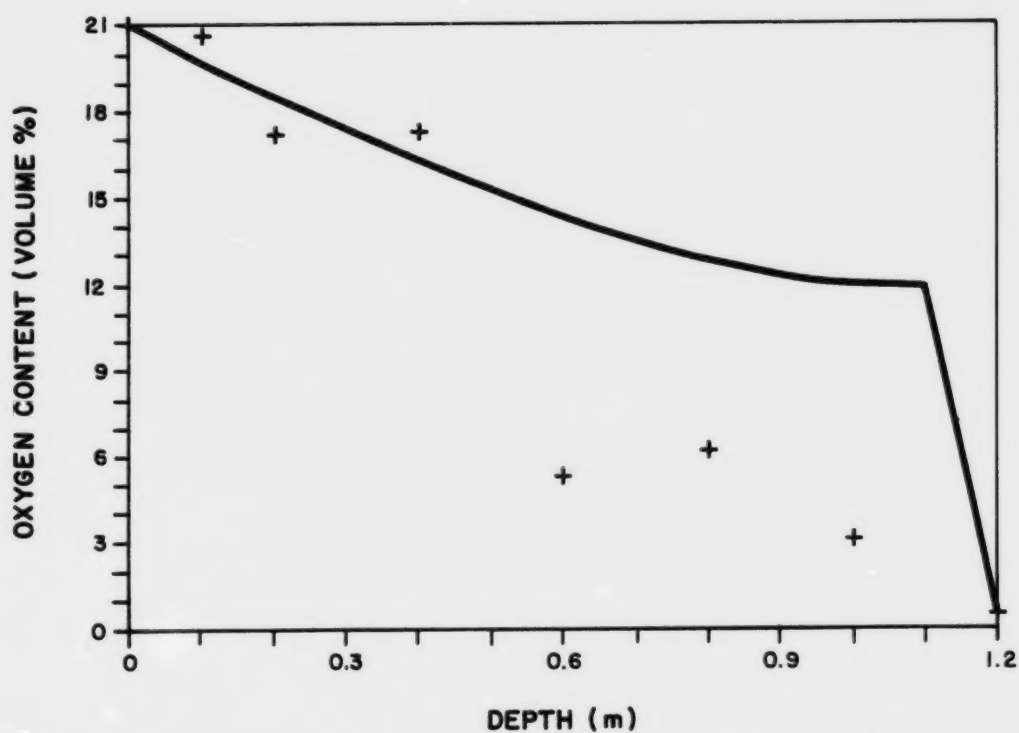
FIGURE C.2
OXYGEN PROFILE
FOR PIEZOMETER PN - 8
(OXYGEN MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
+ EXPERIMENTAL RESULTS BY GOLDER ASSOCIATES (1981)

FIGURE C.3
OXYGEN PROFILE
FOR PIEZOMETER PN-3
(OXYGEN MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
+ EXPERIMENTAL RESULTS OF GOLDER ASSOCIATES (1981)

Table C.5.1
Sensitivity Analysis
on the Partial Oxygen Pressure

SENSITIVITY OF INPUTS ON P02

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.767E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.454E-01	0.194E+00
2	0.587E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.752E-01	0.182E+00
LAYER 5 FOR MONTH 13								
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.206E-11	0.190E+00
2	0.885E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.228E-01	0.198E+00
3	0.688E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.572E-01	0.184E+00
4	0.107E+00	-	VI	0.100E-02	0.500E-02	0.100E-01	0.173E+00	0.193E+00
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.189E-13	0.351E-01
2	0.954E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.865E-15	0.188E-13
3	0.750E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.434E-14	0.174E-13
4	0.123E+00	-	VI	0.100E-02	0.500E-02	0.100E-01	0.162E-13	0.185E-13
LAYER 1 FOR MONTH 18								
1	0.216E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.160E+00	0.205E+00
2	0.125E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.181E+00	0.207E+00
LAYER 5 FOR MONTH 18								
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.273E-11	0.192E+00
2	0.523E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.902E-01	0.189E+00
3	0.407E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.109E+00	0.184E+00
4	0.358E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.118E+00	0.184E+00
5	0.134E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.160E+00	0.185E+00
6	0.132E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.161E+00	0.186E+00
LAYER 11 FOR MONTH 18								
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.535E-14	0.565E-04
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.170E-13	0.347E-02
1	0.100E+01	+	V6	0.600E-02	0.300E-01	0.600E-01	0.170E-13	0.739E-09
2	0.456E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.852E-14	0.157E-13
3	0.410E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.924E-14	0.157E-13
4	0.160E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.135E-13	0.161E-13
5	0.137E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.136E-13	0.158E-13
6	0.101E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.145E-13	0.161E-13
LAYER 1 FOR MONTH 121								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	0.196E+00
2	0.355E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.100E+00	0.155E+00
3	0.168E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.149E+00	0.179E+00
4	0.129E+00	-	KFEEDH	0.127E+01	0.398E+02	0.127E+04	0.163E+00	0.187E+00
5	0.107E+00	-	VI	0.100E-02	0.500E-02	0.100E-01	0.170E+00	0.191E+00
LAYER 5 FOR MONTH 121								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	0.373E-02
2	0.431E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.866E-01	0.152E+00
3	0.197E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.144E+00	0.179E+00

SENSITIVITY OF INPUTS ON P02

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
4	0.150E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.161E+00	0.189E+00
5	0.125E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.169E+00	0.193E+00

LAYER 11 FOR MONTH 121

1	0.992E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.193E-13	0.230E-11
2	0.483E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.735E-14	0.142E-13
3	0.216E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.133E-13	0.169E-13
4	0.163E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.150E-13	0.179E-13
5	0.143E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.158E-13	0.184E-13
6	0.104E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.166E-13	0.185E-13
7	0.102E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.160E-13	0.178E-13

LAYER 1 FOR MONTH 126

1	0.355E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.131E+00	0.204E+00
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LAYER 5 FOR MONTH 126

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	0.173E-13
2	0.180E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.148E+00	0.181E+00
3	0.134E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.145E+00	0.168E+00
4	0.126E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.164E+00	0.188E+00
5	0.111E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.163E+00	0.183E+00
6	0.103E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.163E+00	0.182E+00

LAYER 11 FOR MONTH 126

1	0.993E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.170E-13	0.232E-11
2	0.226E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.118E-13	0.153E-13
3	0.221E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.130E-13	0.167E-13
4	0.199E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.112E-13	0.140E-13
5	0.159E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.133E-13	0.158E-13
6	0.147E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.133E-13	0.156E-13
7	0.125E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.135E-13	0.155E-13

APPENDIX D: PYRITE OXIDATION (MODULE IV)

D.1 Theoretical Background

D.1.1 Overall Rate Equation

Numerous investigations into the mechanisms and kinetics of bacteria-assisted pyrite oxidation have been carried out (MacDonald and Clark, 1970; Dugan and Randles, 1971; Wong et al., 1974; Hoffmann et al., 1981; Brown and Forshaug, 1983; Jaynes et al., 1984) For a heterogeneous reaction, such as pyrite oxidation, the specific reaction rate is normally defined (Aris, 1969) as:

$$R = \frac{-1}{A} \frac{dN_p}{dt} \quad (D.1.1)$$

where

R = the specific reaction rate ($\text{mol} \cdot \text{m}^{-2} \cdot \text{mth}^{-1}$)

A = the tailings particle surface area (m^2)

t = time (mth)

N_p = amount of pyrite (mol)

Taking the stoichiometry of equation (B.1.1) into consideration the specific reaction rate can be rewritten in terms of the disappearance of oxygen or the formation of ferrous iron or sulphate:

$$R = \frac{-1}{A} \frac{dN_p}{dt} = \frac{-1}{3.75A} \frac{dN_{O_2}}{dt} = \frac{1}{A} \frac{dN_{Fe^{2+}}}{dt} = \frac{1}{2A} \frac{dN_{SO_4^{2-}}}{dt} \quad (D.1.2)$$

In the above equation the rate of pyrite oxidation can be expressed as:

$$R = \frac{-1}{A} \frac{dN_p}{dt} = \frac{-k N_p}{A} \quad (D.1.3)$$

where

k = the reaction rate constant (mth^{-1})

Rearranging equation (D.1.3) and solving for the pyrite concentration in the solid phase results in:

$$N_{p,t} = N_{p,t_0} \exp(-k t) \quad (\text{D.1.4})$$

where

N_{p,t_0} = the initial amount of pyrite at time ' t_0 ' (mol)

$N_{p,t}$ = amount of pyrite at time ' t ' (mol)

Those factors which have an important influence on the rate of pyrite oxidation described by the above equations are oxygen transport and pyrite surface area. The significance of these factors is discussed below.

D.1.2 Oxygen Transport

There are two mechanisms by which oxygen can be transported; convective transport and diffusion. On the micro-level diffusion of oxygen through the stagnant water film overlying the pyritic surface is considered to be a limiting transport step. Discussion of oxygen transport on the macro level, i.e. between soil layers, is included in Appendix C.

The rate of oxygen diffusion through the stagnant film can be expressed in terms of the concentration gradient and diffusive transport coefficient as follows:

$$\frac{dC}{dt} = -D_e \frac{d^2C}{dx^2} \quad (\text{D.1.5})$$

where

C = concentration of oxygen in the liquid phase (mol.m^{-3})

t = time (mth)

$\frac{d^2C}{dx^2}$ = rate of change of the oxygen concentration gradient in the fluid along the direction of transport (mol.m^{-5})

D_e = effective diffusivity ($\text{m}^2.\text{mth}^{-1}$)

x = distance of penetration into the water film (m)

The film, water or air, through which the oxygen passes plays a significant role in determining the flux. For example, the diffusivity of oxygen through air at 25°C and 1 atm pressure is $53.4 \text{ m}^2.\text{mth}^{-1}$ ($0.206 \text{ cm}^2.\text{s}^{-1}$), whereas through water at 25°C the diffusivity is $4.7 \times 10^{-3} \text{ m}^2.\text{mth}^{-1}$ ($0.18 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$). This comparison indicates that the diffusivity of oxygen in air is slightly more than 10,000 times greater than the diffusivity of oxygen in water (U.S. EPA, 1971).

If one assumes that the water film on a particle is $4 \times 10^{-4} \text{ m}$ thick and that the rate of oxygen utilization in pyrite oxidation is $15 \text{ } \mu\text{g}.\text{hr}^{-1}.\text{g}^{-1}$ (a reasonable rate for finely divided sulfur ball material), the resulting reduction in the mass transfer is approximately 10% (derived from U.S. EPA, 1971).

A second method of estimating the flux of oxygen through a stagnant water film is given by the expression:

$$R = k_L (C_i - C_1) \quad (\text{D.1.6})$$

where

R = the specific reaction rate ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

k_L = overall mass transfer coefficient (m.mth^{-1})

C_i = concentration in liquid phase at the liquid/solid interface (mol.m^{-3})

C_1 = concentration in liquid phase at the outer edge of the film (mol.m^{-3})



The mass transfer coefficient for oxygen transport from the air pore space to the microbe has been described by Myerson (1981) as:

$$K_v = \frac{X_d \mu}{Y_{O_2}(C_1 - C_0)} \quad (D.1.7)$$

where

K_v = volumetric oxygen mass transfer coefficient (mth^{-1})

X_d = bacteria density (g bacterial biomass m^{-3})

Y_{O_2} = oxygen yield coefficient (g bacterial biomass produced mol^{-1} oxygen consumed)

C_1 = the oxygen concentration in solution at saturation ($\text{mol} \text{m}^{-3}$)

C_0 = the actual oxygen concentration in solution ($\text{mol} \text{m}^{-3}$)

μ = the specific growth rate (mth^{-1})

In the Myerson (1981) study the volumetric oxygen mass transfer coefficient required to maintain the oxygen concentration above the critical concentration was found to be $42,700 \text{ mth}^{-1}$ (58.5 hr^{-1}). This K_1 value was for the growth of T. ferrooxidans at pH 2.5 and 28°C .

Limiting Effect of Oxygen on Bacteria Oxidation

As indicated in the overall reaction equation (B.1.1), the growth of aerobic bacteria is influenced by oxygen availability. The reaction rate is not normally limited by the oxygen availability provided that an adequate rate of 1) diffusion from the atmosphere to the pore space of the host material occurs and 2) the mass transfer from the gas phase to the liquid (water) phase is maintained.

Myerson (1981) determined critical oxygen concentrations below which oxygen acts as the limiting substrate in pyrite oxidation. The data indicated that the critical oxygen concentration was quite low, in the liquid phase of

agitated flask experiments, equalling approximately 5 percent ($0.015 \text{ mol.m}^{-3}_{\text{water}}$) of the oxygen concentration at saturation.

Jaynes et al. (1984) defined the inhibition of oxygen as follows:

$$X_{O_2} = 1.0 \quad \text{for } F_{O_2} > 0.01 \quad (\text{D.1.8a})$$

$$X_{O_2} = F_{O_2}/0.01 \quad \text{for } F_{O_2} < 0.01 \quad (\text{D.1.8b})$$

where

X_{O_2} = fraction of peak cell activity as influenced by oxygen concentration (0 to 1)

F_{O_2} = mole fraction of O_2 in gas phase (mol.mol^{-1})

The above relationships were based upon the assumption that the critical oxygen concentration reported by Myerson (1981), 5% of the water saturated level, also applied for the gas phase.

Limiting Effect of Oxygen on Chemical Oxidation

Several different relationships between oxidation rate and concentration of oxygen have been reported in the literature (Van Breemen, 1982; Nordstrom, 1982; Cherry et al., 1983). The conclusion of these studies is that the rate is proportional to the partial pressure of oxygen:

$$R \propto k P_{O_2}^n \quad (\text{D.1.9})$$

where

R = the specific reaction rate ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

k = the rate constant (mth^{-1})

P_{O_2} = partial pressure of oxygen (atm)



n = order of reaction

Suggested fractional order values include 0.8, 2/3 and 1/2 (Lowson, 1982).

In a study by Nicholson (1984) the following relationship for the rate of pyrite oxidation was developed:

$$\log(R_s) = \log(k_c) + 0.59 \log [O_2] \quad (D.1.10a)$$

or

$$\log\left(\frac{R_s}{k_c}\right) = 0.59 \log [O_2] \quad (D.1.10b)$$

where

$[O_2]$ = the percent oxygen saturation (%)

k_c = chemical rate constant ($\text{mg SO}_4 \cdot \text{d}^{-1} \cdot \text{g}^{-1}$)

R_s = rate of pyrite oxidation ($\text{mg SO}_4 \cdot \text{d}^{-1} \cdot \text{g}^{-1}$)

In the development of the equation above, experiments were run in unsaturated columns in which the gas phase passing through each column was maintained at a specified level between 0.01 and 20% oxygen.

The fractional order of the reaction (i.e. 0.59 in equation (D.1.10)) suggests that the rate is controlled by adsorption-type mechanisms in contrast to molecular or atom-transfer processes that would be observed if first-order results were obtained (Cherry et al., 1983).

Jutte (1966) using the Hougen and Watson (1957) adsorption model, derived a rate equation which correlated well with experimental data.

$$R_{O_2} = \frac{k[O_2]}{1 + K_1[O_2] + K_2[I]} \quad (D.1.11)$$

$$1 + K_1[O_2] + K_2[I]$$

Where

R_{O_2} = reaction rate ($\text{mol.m}^{-3}\text{.mth}^{-1}$)

k = reaction rate constant (mth^{-1})

$[O_2]$ = concentration of dissolved oxygen (mol.m^{-3})

K_1 = adsorption equilibrium constant for oxygen on pyrite ($\text{m}^3.\text{mol}^{-1}$)

K_2 = adsorption equilibrium constant for inert material on pyrite
($\text{m}^3.\text{mol}^{-1}$)

$[I]$ = concentration of inert gas (mol.m^{-3})

D.1.3 Surface Area

Several studies have found that on increasing the surface area of the pyritic material, the oxidation rate increases linearly in direct proportion to the increase in area (Hoffmann et al., 1981; Cherry et al., 1983). Hence, the rate of oxidation of pyrite can be described by an apparent first-order dependence on the total reactive surface of pyrite:

$$\frac{-dN_p}{dt} \propto A \quad (\text{D.1.12})$$

where

N_p = amount of pyrite (mol)

A = total reactive surface area (m^2)

t = time period (mth)

In a study by Lowson (1982), rate expressions, under conditions of no product build-up, which incorporated surface area effects, were reviewed. In two of these reference sources, the oxidation rate was expressed as a function of the diameter of the particles. These included the works of Stenhouse and Armstrong (1952):

$$\frac{-dN_p}{dt} \propto \frac{1}{d^2} \quad (\text{D.1.13})$$



where

d = average particle diameter (m)

In other works, the oxidation rate has been expressed as a function of particle size surface area. Some authors (Steger and Desjardins, 1978; Cornelius and Woodcock, 1958; Mathews and Robins, 1974) have chosen to express the oxidation rate as being directly proportional to surface area:

$$\frac{-dN_p}{dt} \propto A_s \quad (D.1.14)$$

whereas Baily and Peters (1976) have related the oxidation rate to the surface area raised to a power:

$$\frac{-dN_p}{dt} \propto A_s^n \quad (D.1.15)$$

where:

n = empirical coefficient

A_s = particle size surface area (m^2)

D.2 Algorithm Development

D.2.1 Overall Reaction Rate

As shown in Appendix B, the rate of pyrite oxidation can be expressed as:

$$\frac{dM}{dt} = \frac{-A_p}{V} (R_1 + R_2) \quad (D.2.1)$$

where

M = moles of pyrite per unit volume of tailings ($mol.m^{-3}$)

R_1 = biological specific reaction rate ($mol.m^{-2}mth^{-1}$)

R_2 = chemical specific reaction rate ($\text{mol.m}^{-2} \text{ mth}^{-1}$)
 A_p = surface area of pyrite (m^2)
 V = volume of tailings (m^3)
 t = time (mth)

The effects of including oxygen limitation and changing surface area in the above expression are discussed below.

D.2.2 Limiting Oxygen Concentration

The limiting effect of oxygen on the biological specific reaction rate can be included in equation (D.2.1) by replacing the term R_1 with:

$$R_{1b} = R_1 \frac{(P_{O_2(i-1)} + P_{O_2(i)})^{0.5}}{L_o + (P_{O_2(i-1)} + P_{O_2(i)})^{0.5}} \quad (\text{D.2.2})$$

where

$P_{O_2(i)}$ = partial pressure of oxygen at i th boundary (atm)
 L_o = limiting oxygen partial pressure (atm)
 R_{1b} = oxygen influenced biological specific reaction rate ($\text{mol.m}^{-2} \text{ mth}^{-1}$)

The influences of oxygen concentration is included in the above equation as a Monod type expression.

The chemical term, R_2 in equation (D.2.1), already includes an oxygen dependence:

$$R_2 = f_p k_c (P_{O_2(i-1)} + P_{O_2(i)})^{0.5} \quad (\text{D.2.3})$$

where:

k_c = chemical reaction rate ($\text{mol.m}^{-2} \text{ mth}^{-1} \text{ atm}^{-1}$)



R_2 = chemical specific reaction rate ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

f_p = pH dependence factor

A first order relationship is assumed in the above expression.

D.2.3 Effect of Particle Size Distribution

It is well documented that the rate of pyrite oxidation is a function of pyrite surface area (Hoffmann et al., 1981; Steger and Desjardins, 1978; Cornelius and Woodcock, 1958; Mathews and Robins, 1974). As oxidation proceeds the surface area of the pyrite particles decreases. The rate at which the pyrite particle "shrinks" as it is depleted through oxidation can be described by the following expression:

$$\frac{dM}{dt} = \left(\rho_p \frac{A_p}{V} \right) \frac{dr}{dt} \quad (\text{D.2.4})$$

where:

ρ_p = moles of pyrite per unit volume of pyrite (mol.m^{-3})

r = average radius of pyrite particles (m)

V = volume of tailings (m^3)

A_p = total surface area of pyrite particle (m^2)

In the above expression the pyrite particles are assumed to be spherical.

An overall rate equation for oxidation of pyrite can be determined by combining equations (D.2.1) and (D.2.4):

$$\frac{\rho_p}{V} A_p \frac{dr}{dt} = \frac{A_p}{V} (R_{1b} + R_2) \quad (\text{D.2.5})$$

or

$$\frac{dr}{dt} = \frac{R_t}{\rho_p} \quad (D.2.6)$$

where

R_t = overall specific reaction rate, (i.e. $R_{1b} + R_2$) ($\text{mol.m}^{-2}.\text{mth}^{-1}$)

Integrating the above expression (assuming R_t is constant over a time period "0 to t") yields:

$$r_0 - r = \frac{R_t t}{\rho_p} \quad (D.2.7)$$

where:

r_0 = initial radius of particles (m)

The significance of equation (D.2.7) is that the radius decreases at a constant rate given by:

$$k_0 = \frac{R_t}{\rho_p} \quad (D.2.8)$$

where:

k_0 = rate constant for oxidation (m.mth^{-1})

It has been shown, that if the number of particles with radius "r" is constant, then:

$$r \propto N_p^{1/3} \quad (D.2.9)$$

Where:

N_p = amount of pyrite (mol)



Dividing equation (D.2.7) by r_0 and substituting in k_0 yields:

$$\frac{r}{r_0} = 1 - k_0 \frac{t}{r_0} \quad (\text{D.2.10})$$

Since $r/r_0 = (N_p/N_{p0})^{1/3}$

the following expression results:

$$\left(\frac{N_p}{N_{p0}}\right)^{1/3} = 1 - \frac{k_0 t}{r_0} \quad (\text{D.2.11})$$

or

$$N_p = N_{p0} \left[1 - \left(\frac{k_0 t}{r_0} \right) \right]^3 \quad (\text{D.2.12})$$

where:

N_{p0} = the initial amount of pyrite (mol)

The above equation applies if particles have a characteristic initial radius, " r_0 ", and the number of particles (if more than a single particle) remains constant.

In tailings, particle size is distributed. Typical distributions are given in Figure D.1. Let us define $F(r)$ as the fraction of pyrite particles having a radius less than a given value, r . Furthermore, the maximum radius is defined as one half of the observed maximum grain size. The cumulative grain size distribution function $F(r)$ can be related to the maximum radius as follows:

$$F(r) = x \left(\frac{r}{r_m} \right)^\alpha + y \left(\frac{r}{r_m} \right)^\beta \quad (\text{D.2.13})$$

where

$F(r)$ = fraction of pyrite particles having a radius less than a given value, r

r = radius of particle (m)

r_m = maximum radius; defined as one-half of the observed maximum grain size (m)

x, y, α, β = Pareto distribution function coefficients

Since the particle radius cannot exceed the maximum value (r_m), it follows that:

$$x + y = 1 \quad (D.2.14)$$

Equation (D.2.13) with the constraint expressed by equation (D.2.14) is known as the Pareto distribution function. The parameters of the function (x, y, α, β) can assume any value but often are not integers. It can be easily shown (see equation (D.2.14)) that if x is greater than unity, y must be negative for positive values of α and β . Furthermore, the cumulative distribution function, $F(r)$, cannot have an extreme (either maximum or minimum) within the interval $0 < r/r_m < 1$. This condition is satisfied by the following inequality:

$$\frac{x \alpha}{\beta (x - 1)} \geq 1 \quad (D.2.15)$$

The characteristic parameter values are determined by statistical curve fitting procedures. Since the oxidation of pyrite is dependent on the surface area and the surface area per unit mass is inversely related to the particle radius, the curve fitting (i.e. parameter estimation) is biased toward the smaller particle size.

Employing the particle size distribution presented in Figure D.1 and a statistical curve fitting procedure results in the following cumulative size distribution function.



$$F(r) = 2 \left(\frac{r}{1.25 \times 10^{-4}} \right)^{0.9} - 1 \left(\frac{r}{1.25 \times 10^{-4}} \right)^{1.8} \quad (D.2.16)$$

where:

r = radius of spherical particles (m)

$r_m = 1.25 \times 10^{-4}$ (m)

$x = 2$

$y = -1$

$\alpha = 0.9$

$\beta = 1.8$

A detailed description of the method of determining the Pareto coefficients is outlined in Section D. 3, Particle Size Distribution.

Assuming that equation (D.2.13) indeed describes the cumulative size distribution in tailings, the size distribution density Function, $f(r)$, is given by:

$$f(r) = \frac{x\alpha}{r_m} \left(\frac{r}{r_m} \right)^{\alpha-1} + \frac{y\beta}{r_m} \left(\frac{r}{r_m} \right)^{\beta-1} \quad (D.2.17)$$

where

$f(r)$ = size distribution density function.

Equation (D.2.17) describes the fraction of tailings having a radius between r and $r + dr$. With the use of this equation we can calculate a weighted average radius for the tailings, which is given by the first moment of the distribution density function:

$$r_{avg} = \int_0^R r f(r) dr = r_m \left(\frac{x\alpha}{1+\alpha} + \frac{y\beta}{1+\beta} \right) \quad (D.2.18)$$

Note that r_{avg} refers to the average radius at initial conditions (i.e. at $t=0$). For the distribution on Figure D.1, ($x=2, y=-1$) $\alpha = 0.9$ and $\beta = 1.8$ the average radius is:

$$r_{avg} = 125 \times 10^{-4} \left(\frac{1.8}{1.9} - \frac{1.8}{2.8} \right) = 3.8 \times 10^{-5} \text{m} \quad (\text{D.2.19})$$

Hence, the average particle size = $7.6 \times 10^{-5} \text{m}$. This is about the 50th percentile of the solid line in Figure D.1.

We may also note at this point, that for any particle radius (r), the surface area per unit mass is given by:

$$a = \frac{3}{\rho_p r} \quad (\text{D.2.20})$$

where:

a = surface area per unit mass ($\text{m}^2 \cdot \text{mol}^{-1}$)

Let $M_{r,t}$ be the moles of pyrite per unit volume of tailings (at time t) that possessed an initial radius " r_0 ". In analogy to equation (D.2.1), the rate of oxidation of this pyrite particle fraction is as follows:

$$\frac{dM_{r,t}}{dt} = -a R_t M_{r,t} = -3 \frac{R_t}{\rho_p} \frac{M_{r,t}}{r} \quad (\text{D.2.21})$$

where:

r = the radius of the particle at any time " t " (m)

ρ_p = moles of pyrite per unit volume of pyrite ($\text{mol} \cdot \text{m}^{-3}$)

It has been shown that if the environmental conditions are constant (equations (D.2.9) and (D.2.8)), the radius decreases at a constant rate k_0 , i.e.:



$$r = r_0 - k_0 t \quad (D.2.22)$$

where

$$k_0 = \frac{R_t}{\rho_p} \quad (\text{m.mth}^{-1})$$

Substituting equation (D.2.22) into equation (D.2.21) and integrating between $t=0$ to $t=t$ gives:

$$\ln \left(\frac{M_{r,t}}{M_{r,0}} \right) = 3 \ln \left(\frac{r - k_0 t}{r_0} \right)$$

or

$$M_{r,t} = M_{r,0} \left(\frac{r - k_0 t}{r_0} \right)^3 \quad (D.2.23)$$

for $r \geq k_0 t$.

For initial radius $r \leq 0$, of course, $M_{r,t} = 0$, since the radius cannot assume a negative value. The initial radii in tailings however, are distributed as given by the size distribution density function (equation (D.2.17)). The total mass of pyrite per unit volume of tailings at any time "t" (M_t) is given by integrating for all initial radii, i.e.:

$$M_t = M_0 \int_0^{r_m} \left(\frac{r - k_0 t}{r_0} \right)^3 \left[x \alpha \left(\frac{r}{r_m} \right)^{\alpha-1} + y \beta \left(\frac{r}{r_m} \right)^{\beta-1} \right] \frac{dr}{r_m} \quad (D.2.24)$$

where

M_0 = initial pyrite concentration in moles per unit volume of tailings (mol.m^{-3}).

Noting that the integral is zero for any $r \leq k_0 t$, the solution of equation (D.2.23) is given as the following polynomial expression:

$$M_t = M_0 \left[1 + a_1 \left(\frac{k_0 t}{r_m} \right)^\alpha + a_2 \left(\frac{k_0 t}{r_m} \right)^\beta + a_3 \left(\frac{k_0 t}{r_m} \right) + a_4 \left(\frac{k_0 t}{r_m} \right)^2 + a_5 \left(\frac{k_0 t}{r_m} \right)^3 \right] \quad (D.2.25)$$

where:

r_m = the initial maximum radius and $k_0 t \leq r_m$

$$a_1 = -x \left(1 - \frac{3\alpha}{\alpha-1} + \frac{3\alpha}{\alpha-2} - \frac{\alpha}{\alpha-3} \right)$$

$$a_2 = y \left(1 - \frac{3\beta}{\beta-1} + \frac{3\beta}{\beta-2} - \frac{\beta}{\beta-3} \right)$$

$$a_3 = \left(-\frac{3x\alpha}{\alpha-1} - \frac{3y\beta}{\beta-1} \right)$$

$$a_4 = \frac{3x\alpha}{\alpha-2} - \frac{3y\beta}{\beta-2}$$

$$a_5 = -\left(\frac{x\alpha}{\alpha-3} - \frac{y\beta}{\beta-3} \right)$$

Once the pyrite concentration has been determined the relationship between surface area and volume of tailings can be determined for any time.

$$\alpha_p = -\frac{M_0}{\rho_p r_m} \left[a_1 \alpha \left(\frac{k_0 t}{r_m} \right)^{\alpha-1} + a_2 \beta \left(\frac{k_0 t}{r_m} \right)^{\beta-1} + a_3 + 2 a_4 \left(\frac{k_0 t}{r_m} \right) + 3 a_5 \left(\frac{k_0 t}{r_m} \right)^2 \right] \quad (D.2.26)$$

where

$$\begin{aligned} \alpha_p &= \text{surface area of pyrite per unit volume of tailings (m}^2\text{.m}^{-3}\text{)} \\ \rho_p &= \text{pyrite density (mol.m}^{-3}\text{)} \end{aligned}$$

The parameter α_p can then be used to determine the pyrite surface area:

$$A_s = \alpha_p V_t \quad (D.2.27)$$

where

$$\begin{aligned} A_s &= \text{surface area of pyrite (m}^2\text{)} \\ V_t &= \text{volume of tailings (m}^3\text{)} \end{aligned}$$

It can be shown that for an initial particle size distribution having $r_m = 1.25 \times 10^{-4}$ $\alpha = 0.9$, $\beta = 1.8$, $x = 2$ and $y = -1$:

$$\begin{aligned} a_1 &= -51.948052 \\ a_2 &= -31.250000 \\ a_3 &= +60.750000 \\ a_4 &= +22.090909 \\ a_5 &= -0.642897 \end{aligned}$$

and

$$\begin{aligned} \frac{M_t}{M_0} = 1 + a_1 \left(\frac{k_0 t}{1.25 \times 10^{-4}} \right)^{0.9} + a_2 \left(\frac{k_0 t}{1.25 \times 10^{-4}} \right)^{1.8} + a_3 \left(\frac{k_0 t}{1.25 \times 10^{-4}} \right)^2 + a_4 \left(\frac{k_0 t}{1.25 \times 10^{-4}} \right)^3 \\ + a_5 \left(\frac{k_0 t}{1.25 \times 10^{-4}} \right)^4 \end{aligned}$$

D.3 Parameter Distributions

The basis for the values of the parameters employed in the pyrite oxidation module are discussed in this section. Also discussed are the probability distributions selected to characterize the uncertainty in the parameter values. Table D.3.1 lists the probability distribution types and descriptors

FIGURE D.1
TYPICAL RANGE OF GRAIN SIZE DISTRIBUTION
FOR ACID GENERATING TAILINGS

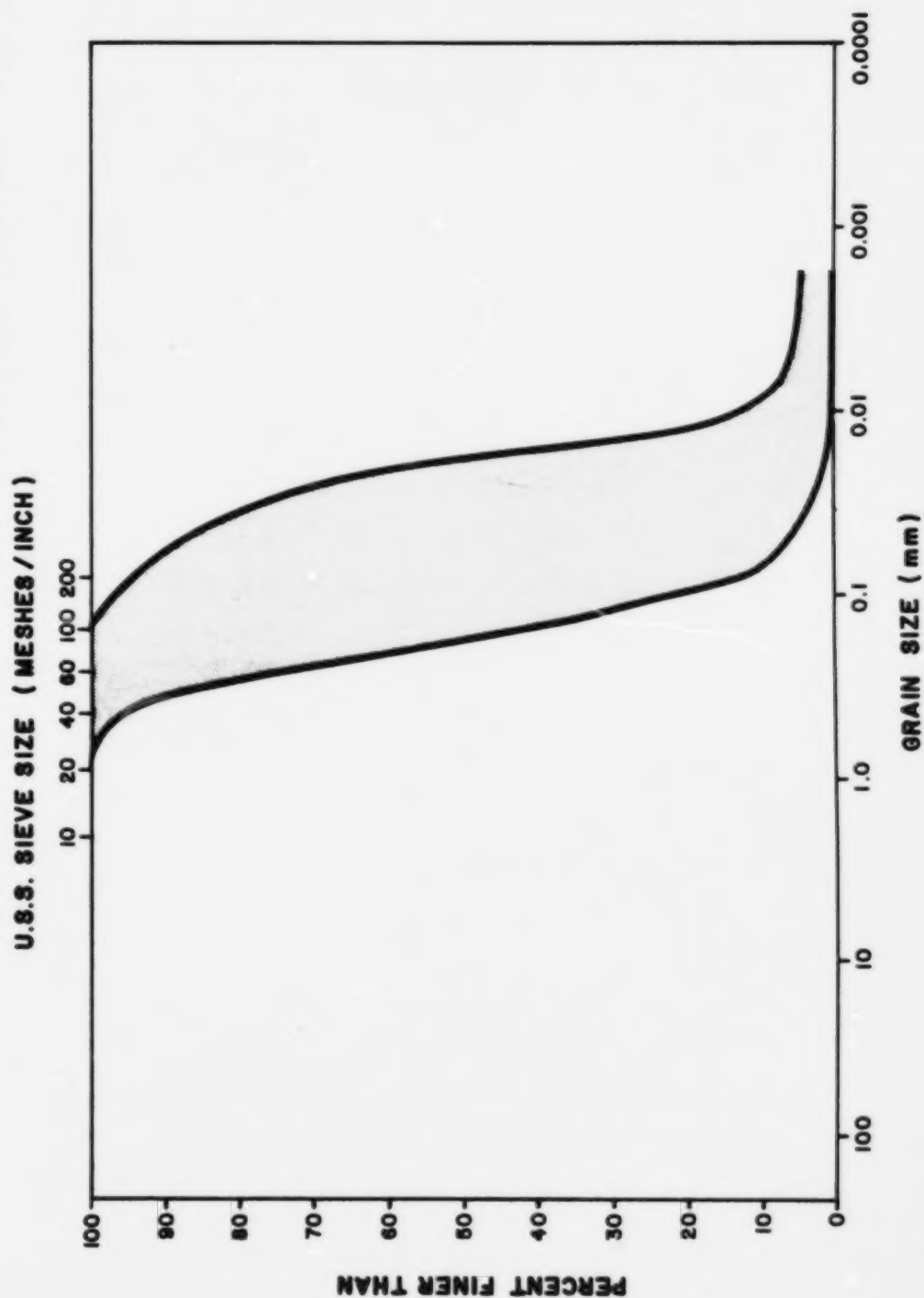


Table D.3.1
PYRITE MODULE PARAMETERS

Model Symbol	Description	Units	Nominal Value	Probability Distributions	Module Source	Computer Symbol
A_s	Surface area of pyrite	(m^2)	calculated	calculated	Pyrite	AS(i,t)
f_{pH}	pH dependence factor	(unitless)	calculated	calculated	Kinetics	FPH
x_{pyr}	Fraction of pyrite in tailings	$kg.kg^{-1}$	0.06	U(0.048,0.072)	Input	XPYR
k_0	Rate constant	($m.mth^{-1}$)	calculated	calculated	Pyrite	K(i,t)
K_c	Chemical Rate Constant	($mol.m^{-2}.mth^{-1}.atm^{-1}$)	4.72×10^7	T($4.7 \times 10^6, 4.72 \times 10^7, 4.72 \times 10^8$)	Input	KCONT
L_c	Capillary layer	unitless	calculated	calculated	Initial	LC
L_0	Limiting oxygen concentration	(atm)	0.01	C(0.01)	Input	L02
L_s	Layer at which saturated zone starts	unitless	21	C(21)	Input	LS
M	Amount of pyrite per unit volume of tailings	($mol.m^{-3}$)	calculated	calculated	Pyrite	PYR(i,t)
N_p	Amount of pyrite	(mol)	calculated	calculated	Pyrite	NP(i,t)
P_{O2}	Partial pressure of oxygen	(atm)	calculated	calculated	Oxygen	P02(i,t)
ρ_p	Molar density of pyrite	($mol.m^{-3}$)	41670	C(41670)	Input	DP
R_1	Biological specific reaction rate	($mol.m^{-2}.mth^{-1}$)	calculated	calculated	Kinetic	R1(i,t)
R_{1b}	Oxygen influenced biological specific reaction rate	($mol.m^{-2}.mth^{-1}$)	calculated	calculated	Pyrite	R1B(i,t)
R_2	Chemical specific reaction rate	($mol.m^{-3}.mth^{-1}$)	calculated	calculated	Kinetic	R2(i,t)
r_m	Maximum radius	(m)	1.25×10^{-4}	C(1.25×10^{-4})	Input	RMAX
	Rpyr Overall reaction rate per volume of tailings	($mol.m^{-3}.mth^{-1}$)	calculates	calculate	pyrite	RPYR
R_t	Overall specific reaction rate	($mol.m^{-2}.mth^{-1}$)	calculated	calculated	Pyrite	RT(i,t)
x	Paretto Coefficient	unitless	2	C(2)	Input	A1
y	Paretto Coefficient	unitless	-1	C(-1)	Input	B1

Table D.3.1 cont'd

α	Empirical parameter for particle distribution	unitless	0.9	C(0.9)	Input	AL
α_p	Surface areas of pyrite per unit volume of tailings	($m^2.m^{-3}$)	calculated	calculated	Pyrite	ALPHAP(i,t)
β	Empirical parameter for particle distribution	unitless	1.8	C(1.8)	Input	BE

NOTE:

i Indicates the particular layer
t Indicates overall time period
m Indicates the month of the year

Key to Probability Distributions:

C - Constant (single value)
T - Triangular (min., mode, max.)
U - Uniform (min., max.)

and the computer source symbols assigned to the parameters.

D.3.1 Limiting Oxygen Concentration

The limiting oxygen concentration (L_0) is defined as the concentration below which oxygen acts as a limiting substrate thus limiting the rate of bacterial growth. Myerson (1981) reported a limiting oxygen concentration of approximately 5% of the bulk oxygen concentration at saturation for the growth of T. ferrooxidans at a pH of 2.5. For this study, the 5% value was assumed to be valid for the gas phase concentration. Hence, a limiting oxygen concentration of 0.01 atm was used.

D.3.2 Particle Size Distribution

Tailings solids are usually not uniform in size, rather, they possess a characteristic size distribution. This grain size distribution is measured by sieving and hydrometer sedimentation techniques and the results of the analyses are reported as aggregate mass fractions having a grain size less than a given diameter. Pyrite occurs as distinct particles in the tailings solids. Previous size classification studies have indicated that the grain size distribution of pyrite is similar to that for the tailings mass as a whole, hence, the characteristic size distribution of the tailings is applicable to pyrite as well.

It is evident in all size classification analyses, that, for a given tailings mass, the grain size is constrained by a characteristic maximum particle size. This maximum particle size is dependent on the milling practice. The size distribution in a tailings area is dependent on the location of tailings discharge. Slimes possess a lower maximum particle size than sandy tailings and will typically settle farthest from the discharge point.

The maximum grain size may be used as a parameter for modelling the size distribution of tailings solids. Furthermore, a spherical symmetry of tailings grains can be assumed so that the characteristic radii of the tailings solids



may be taken as one-half of the grain size as determined by the classification methods.

The grain size distribution employed in the model is illustrated in Figure D.1. This grain size distribution was obtained for Stanrock tailings by Golder Associates (1981). Since the value for the parameter β in equation (D.2.13) is large in comparison to the others, for small grain size the second term in equation (D.2.13) can be neglected. In this case, the parameter " α " can be obtained by linear regression of the following equation:

$$\ln F(r) = \alpha \ln r + K \quad (D.3.1)$$

where

$F(r)$ = the observed cumulative size distribution

r = radius of particle (μm)

K = constant

In the present case, the maximum radius was estimated to be $200 \mu\text{m}$ ($2.0 \times 10^{-4}\text{m}$) and the calculated regression coefficient, α , was found to be 0.68 for particles less than $25 \mu\text{m}$ ($2.5 \times 10^{-5}\text{m}$) radius. From the regression analysis it was evident that the parameter " x " is greater than unity, hence " y " must be a negative value. The "best" estimates of x and β were found by minimizing the total sum of squares (ss) for the entire data set:

$$ss = \sum \left[\frac{f(r_0)}{\left(\frac{r_0}{r_m}\right)^\alpha} - x + (1-x) \left(\frac{r}{r_m}\right)^x \right]^2 \quad (D.3.2)$$

where

$$r = \beta - \alpha$$

The minimum of equation (D.3.2) occurred at $x=1.55$ and at the maximum permissible value of β (see equation (D.2.15)) giving the following equation for the continuous size distribution function:

$$F(r) = 1.55 \left(\frac{r}{200} \right)^{0.68} - 0.55 \left(\frac{r}{200} \right)^{1.90} \quad (D.3.3)$$

In Table D.3.2 the "observed" grain size distribution is compared with the prediction given by equation (D.3.3). The "observed" grain size was obtained by smoothing the experimental results. As shown in Table D.3.2 the continuous distribution function given by equation (D.3.3) approximates the actual distribution particularly well for less than 82.5 μm size. Although the differences between observed and predicted size distribution are more pronounced at particle radii greater than 80 μm , these larger particles have little effect on the pyrite oxidation kinetics. For example, the contribution of particles to the pyrite oxidation rate in the 90 to 100 percentile range (greater than 100 μm radius) is less than 2% of those in the 0 to 10 percentile fraction.

Once the cumulative size distribution function is established, the fraction of pyrite remaining after some time "t" can be obtained.

It has been shown that zero order surface controlled reactions give rise to a linear change in particle radius. If " k_0 " is defined as this linear rate of decrease in particle radius ($\mu\text{m.mth}^{-1}$) during a time period Δt , it follows, that the total change in particle radius at time "t" is:

$$\Delta r = k_0 \Delta t$$

Pyrite particles having a radius less than Δr have been completely oxidized. The remaining mass fraction of pyrite is given by equation (D.2.25).



D.4 Algorithm Calibration/Validation

In this section the predicted influence of oxygen concentration and surface area are compared to experimental data and predictions of other models.

D.4.1 Oxygen

The transport of oxygen can be a rate limiting step in the oxidation of pyrite. Figure D.2 presents the predicted biological pyrite oxidation rate as a function of oxygen partial pressure. The model predicts a sharp decrease in the rate of pyrite oxidation for oxygen concentrations below approximately 0.05 atm.

Also presented on the figure is the prediction from Jaynes et al. (1984) model; discussed in Section D.1.2. The Jaynes et al. (1984) model assumes that oxygen partial pressures greater than 0.01 atm do not affect the biological rate of pyrite oxidation while below this value the effect is linear.

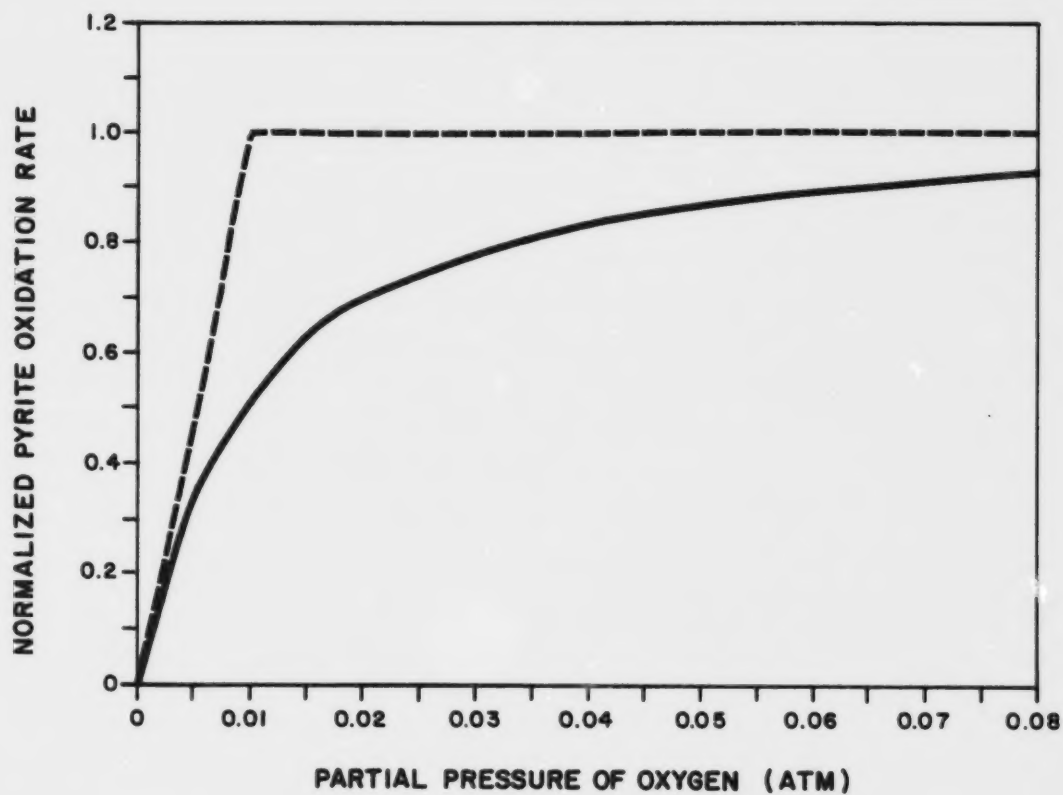
The influence of oxygen concentration on the chemical oxidation rate is presented in Figure D.3. The model predicts slightly lower values than the experimental data of Cherry et al. (1983).

D.4.2 Surface Area

To verify the adequacy of the presented continuous particle size method in Section D.2.3, a second solution employing a discrete particle size method was used. This latter solution places the particle distributions into bins and calculates the pyrite depletion per bin.

To model tailings pyrite oxidation by discrete particle size distribution, we must first determine the particle radius corresponding to a given cumulative size distribution. Substituting $x=2$ and $y=-1$ in equation (D.2.13) we get:

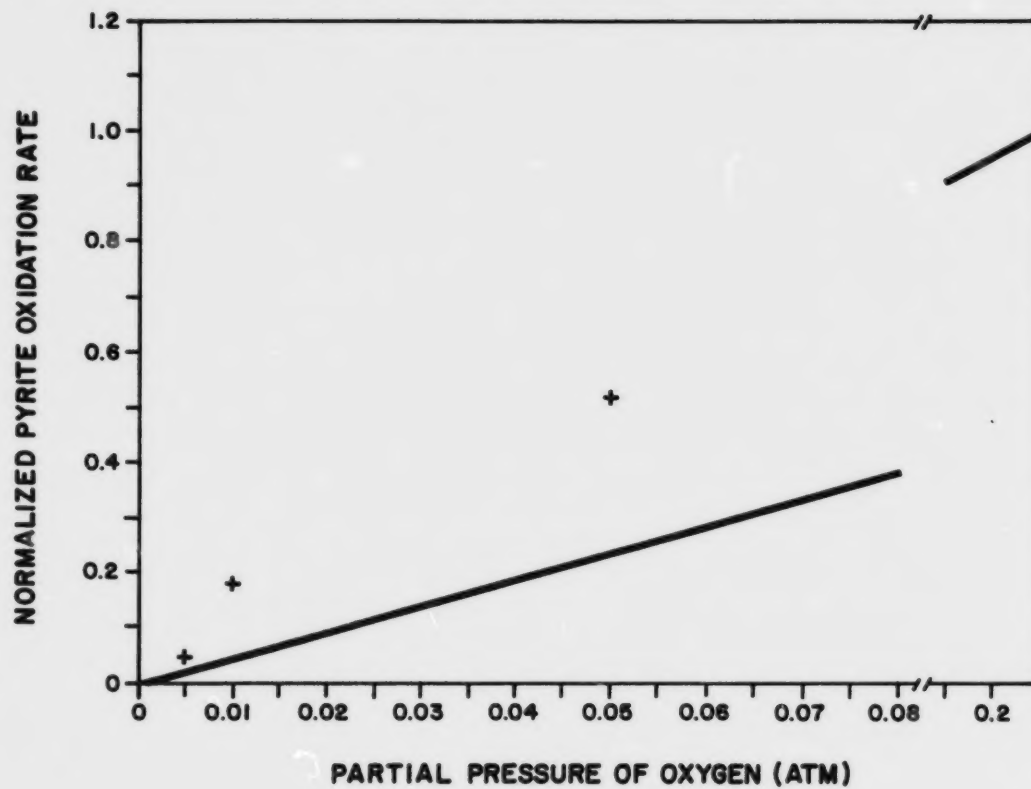
FIGURE D.2
EFFECT OF OXYGEN
ON BIOLOGICAL RATE
(PYRITE MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
- - - MODEL PREDICTED RESULTS OF JAYNES et al (1984)

FIGURE D.3
EFFECT OF OXYGEN
ON CHEMICAL RATE
(PYRITE MODULE)



LEGEND:

- MODEL PREDICTED RESULTS
- + EXPERIMENTAL RESULTS OF CHERRY et al (1983)

Table D.3.2

OBSERVED AND CALCULATED GRAIN SIZE DISTRIBUTION
FOR STANROCK TAILINGS

Particle Radius (μm)	F Observed	F Calculated
1.2	0.05	0.05
4.0	0.10	0.11
7.0	0.15	0.16
11.0	0.20	0.21
16.0	0.25	0.27
22.0	0.30	0.34
35.0	0.40	0.45
45.0	0.50	0.53
55.0	0.60	0.60
67.5	0.70	0.67
82.5	0.80	0.75
100.0	0.90	0.82
200.0	1.00	1.00

$$F(r) = 2 \left(\frac{r}{r_m} \right)^\alpha - \left(\frac{r}{r_m} \right)^\beta \quad (D.4.1)$$

where

F = the cumulative mass fraction ($0 \leq F \leq 1$)

The average particle size in a "bin" corresponding to mass fraction between F and $F + \Delta F$ is given by:

$$r_{\Delta F} = \frac{\int_{r_F}^{r_{F+\Delta F}} \frac{r}{r_m} \left[2\alpha \left(\frac{r}{r_m} \right)^{\alpha-1} - \beta \left(\frac{r}{r_m} \right)^{\beta-1} \right] dr}{\Delta F} \quad (D.4.2)$$

Using the distribution density function with $\alpha = 0.9$, $\beta = 1.8$, $r_m = 125 \mu$, 10 bins can be constructed ($\Delta F = 0.1$) with average radii given as follows:

ΔF	$r_{\Delta F} (\mu m)$
0.1	2.16
0.1	7.38
0.1	13.41
0.1	20.25
0.1	27.80
0.1	36.46
0.1	46.26
0.1	57.96
0.1	72.81
0.1	96.11

The pyrite mass fraction in any bin remaining after some time, t is given by:



$$\frac{\Delta F_t}{\Delta F_0} = \left[1 - \frac{k_0 t}{r} \right]^3 \quad \text{if } r \geq k_0 t \quad (\text{D.4.3})$$

and

$$\frac{\Delta F_t}{\Delta F_0} = 0 \quad \text{if } r < k_0 t \quad (\text{D.4.4})$$

where

ΔF_0 = initial bin size

The mass ratio of pyrite remaining at any time "t" is given by the sum of "bins" as follows:

$$\frac{M_t}{M_0} = \Delta F_0 \sum_{i=1}^n \left[1 - \frac{k_0 t}{r_{\Delta F}} \right]^3 \quad (\text{D.4.5})$$

To compare the predictions of the two methods, the reduction of radii by selected values of " $k_0 t$ " (i.e. $k_0 t = 1\mu\text{m}$, $2\mu\text{m}$, etc) was used. The mass fraction of pyrite remaining was calculated using either equation (D.2.25) (Continuous Particle Size Distribution) or equation (D.4.5) (Discrete Particle Size Distribution). The results are summarized in Table D.4.1.

The predicted values are essentially identical. This indicates that the polynomial expression (equation (D.2.25)) based on a continuous size distribution function can be used to predict the time dependence of pyrite oxidation. On the other hand, 10 bins are sufficient to predict the pyrite fraction, should the discrete particle size method be used.

In applying the above for tailings oxidation, the value of " k_0 ", varies seasonally. However, the equations are applicable by replacing the term " $k_0 t$ " in equation (D.2.25) or equation (D.4.5) by:

$$dt = \sum_0^t k_t \Delta t \quad (D.4.6)$$

where:

$$k_t = \frac{R_t}{\rho_p} = \frac{\mu X_p}{Y_{x/s} \rho_p}$$

μ = specific growth rate of I. ferrooxidans, which is a function of temperature, pH, moisture content, etc., and hence time of year.

D.5 Sensitivity/Uncertainty Analysis

The results of a sensitivity/uncertainty analysis are presented in Tables D.5.1 and D.5.2 for the parameters calculated in the pyrite oxidation module. The calculated parameters include the amount of pyrite remaining and the overall specific reaction rate. Only the input parameters which have a sensitivity index value, SI, greater than 0.1 are listed in each case. The restricted length of the lists is sufficient however, to identify the most important parameters.

Table D.4.1

MASS FRACTION OF PYRITE REMAINING AT TIME t

$k_0 t$ (μm)	Continuous Size Distribution Method	Discrete Particle Size Distribution Method
	$\frac{M_t}{M_0}$	$\frac{M_t}{M_0}$
1	0.809	0.808
2	0.703	0.701
5	0.503	0.503
10	0.320	0.320
15	0.213	0.214
20	0.145	0.146
25	0.100	0.100
30	0.069	0.069
35	0.047	0.047
40	0.032	0.032

Table D.5.1
Sensitivity Analysis
on the Amount of Pyrite Remaining

SENSITIVITY OF INPUTS ON PYR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.320E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.510E+03	0.750E+03
2	0.277E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.468E+03	0.648E+03
3	0.131E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.554E+03	0.637E+03
LAYER 5 FOR MONTH 13								
1	0.334E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.513E+03	0.769E+03
2	0.132E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.562E+03	0.648E+03
3	0.111E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.570E+03	0.641E+03
LAYER 1 FOR MONTH 18								
1	0.329E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.434E+03	0.647E+03
2	0.287E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.507E+03	0.711E+03
3	0.255E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.470E+03	0.631E+03
4	0.163E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.531E+03	0.634E+03
LAYER 5 FOR MONTH 18								
1	0.334E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.511E+03	0.767E+03
2	0.170E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.538E+03	0.648E+03
3	0.132E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.555E+03	0.639E+03
LAYER 1 FOR MONTH 121								
1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.471E+03
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.448E+03
2	0.407E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.238E+03	0.402E+03
3	0.303E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.266E+03	0.382E+03
4	0.231E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.304E+03	0.395E+03
5	0.177E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.291E+03	0.353E+03
6	0.151E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.281E+03	0.331E+03
7	0.133E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.292E+03	0.336E+03
8	0.102E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.308E+03	0.343E+03
LAYER 5 FOR MONTH 121								
1	0.647E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.176E+03	0.498E+03
2	0.633E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.180E+03	0.492E+03
3	0.379E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.309E+03	0.497E+03
4	0.359E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.295E+03	0.461E+03
5	0.189E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.393E+03	0.484E+03
6	0.155E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.374E+03	0.443E+03
7	0.153E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.372E+03	0.439E+03
8	0.143E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.362E+03	0.422E+03
9	0.143E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.344E+03	0.401E+03



SENSITIVITY OF INPUTS ON PYR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 126								
1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.467E+03
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.439E+03
2	0.409E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.232E+03	0.393E+03
3	0.317E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.257E+03	0.377E+03
4	0.244E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.296E+03	0.391E+03
5	0.179E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.283E+03	0.345E+03
6	0.157E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.272E+03	0.323E+03
7	0.140E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.283E+03	0.329E+03
8	0.103E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.300E+03	0.335E+03
9	0.101E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.312E+03	0.347E+03
LAYER 5 FOR MONTH 126								
1	0.667E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.165E+03	0.496E+03
2	0.640E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.173E+03	0.480E+03
3	0.379E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.306E+03	0.493E+03
4	0.368E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.292E+03	0.461E+03
5	0.195E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.388E+03	0.483E+03
6	0.158E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.367E+03	0.436E+03
7	0.157E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.335E+03	0.397E+03
8	0.156E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.370E+03	0.438E+03
9	0.149E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.357E+03	0.419E+03

Table D.5.2
Sensitivity Analysis
on the Overall Rate of Pyrite Oxidation

SENSITIVITY OF INPUTS ON RPYR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.989E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.248E-02	0.225E+00
2	0.721E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.945E-02	0.339E-01
3	0.352E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.222E-01	0.343E-01
4	0.212E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.272E-01	0.346E-01
LAYER 5 FOR MONTH 13								
1	0.956E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.507E-02	0.116E+00
2	0.878E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.841E-02	0.688E-01
3	0.445E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.403E-01	0.726E-01
4	0.318E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.557E-01	0.816E-01
5	0.105E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.648E-01	0.724E-01
LAYER 1 FOR MONTH 18								
1	0.979E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.123E+00	0.577E+01
2	0.927E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.456E+00	0.628E+01
3	0.903E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.168E+01	0.173E+02
4	0.858E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.568E+00	0.401E+01
5	0.433E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.405E+01	0.715E+01
6	0.289E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.418E+01	0.587E+01
7	0.224E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.510E+01	0.657E+01
8	0.164E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.514E+01	0.615E+01
9	0.135E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.541E+01	0.625E+01
10	0.123E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.531E+01	0.606E+01
LAYER 5 FOR MONTH 18								
1	0.982E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.732E-01	0.400E+01
2	0.881E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.293E+00	0.247E+01
3	0.438E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.166E+00	0.296E+00
4	0.265E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.236E+00	0.321E+00
5	0.165E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.271E+00	0.325E+00
LAYER 1 FOR MONTH 121								
1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.108E-01
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.657E-03
2	0.533E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.593E-02	0.127E-01
3	0.378E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.822E-02	0.132E-01
4	0.345E+00	-	FALDH	0.100E-01	0.750E-01	0.600E+00	0.838E-02	0.128E-01
5	0.342E+00	+	XPYP	0.480E-01	0.600E-01	0.720E-01	0.660E-02	0.100E-01
6	0.191E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.762E-02	0.942E-02
7	0.173E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.809E-02	0.978E-02
8	0.142E+00	-	KFEQDH	0.127E+01	0.398E+02	0.127E+04	0.750E-02	0.873E-02

SENSITIVITY OF INPUTS ON RPYR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 121								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	0.127E-01
2	0.996E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.826E-03	0.220E+00
3	0.523E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.101E-01	0.212E-01
4	0.348E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.176E-01	0.269E-01
5	0.346E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.178E-01	0.273E-01
6	0.317E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.143E-01	0.209E-01
7	0.245E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.170E-01	0.226E-01
8	0.243E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.147E-01	0.194E-01
9	0.192E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.160E-01	0.199E-01
10	0.133E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.168E-01	0.193E-01
11	0.129E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.152E-01	0.174E-01

LAYER 1 FOR MONTH 126

1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.750E+00
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.103E+01
2	0.443E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.711E+00	0.128E+01
3	0.440E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.833E+00	0.149E+01
4	0.332E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.666E+00	0.996E+00
5	0.260E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.742E+00	0.100E+01
6	0.186E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.804E+00	0.988E+00
7	0.178E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.688E+00	0.838E+00
8	0.143E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.820E+00	0.957E+00
9	0.133E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.848E+00	0.979E+00

LAYER 5 FOR MONTH 126

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.000E+00	0.675E+00
2	0.821E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.275E+00	0.153E+01
3	0.651E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.342E+00	0.979E+00
4	0.562E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.629E+00	0.144E+01
5	0.489E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.357E+00	0.697E+00
6	0.358E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.126E+01	0.196E+01
7	0.333E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.488E+00	0.731E+00
8	0.303E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.471E+00	0.676E+00
9	0.251E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.534E+00	0.712E+00
10	0.149E+00	+	UMAY	0.115E+02	0.130E+02	0.145E+02	0.585E+00	0.687E+00
11	0.133E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.551E+00	0.635E+00
12	0.105E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.603E+00	0.677E+00

APPENDIX E: SOLUTE TRANSPORT MODULE (Module V)

E.1 Theoretical Background

Several models have been developed which predict the transfer of aqueous species in the unsaturated zone, e.g. Femwater/Femwaste (Yeh and Ward, 1979). They are based either upon a steady state or non-steady state approach.

The basic law of mass balance states that for a dissolving substance:

$$V_t \frac{dc}{dt} = q C_{in} - qC + r V \quad (E.1.1)$$

where

- V_t = porewater volume per unit area of tailings ($m^3_{\text{water}} \cdot m^{-2}_{\text{tails}}$)
- C = porewater concentration ($\text{mol} \cdot m^{-3}$)
- q = infiltration rate ($m \cdot \text{mth}^{-1}$)
- C_{in} = concentration of infiltrating rain water ($\text{mol} \cdot m^{-3}$)
- r = dissolution rate ($\text{mol} \cdot m^{-3} \cdot \text{mth}^{-1}$)

If the volume of water, infiltrating concentration, or dissolving rate changes substantially from timestep to timestep, then non-steady state conditions are evaluated. For this work, steady-state conditions are evaluated, resulting in the basic equation being:

$$C = q \frac{C_{in} + r V}{q} \quad (E.1.2)$$

There are two approaches for evaluating transport from layer to layer one is a mixing cell approach, the second is plug flow. In the mixing cell approach, the portion of outflow for one cell to successive cells downstream is specified based upon field data or assumptions. In the plug flow approach, flow is calculated from one cell to the next and then from the second to the third etc. Both approaches give the same results when properly utilized. The



plug flow approach was used herein.

The calculation of aqueous transportation depends upon the presence or absence of equilibrium between the solid phases and solution. Equation (E.1.1) assumes that equilibrium does not exist between solid phase and solution. For conditions where equilibrium does exist, then:

$$C = C_{eq} \quad (E.1.3)$$

where C_{eq} = the calculated equilibrium concentration ($\text{mol}\cdot\text{m}^{-3}$).

Then the mass balance above the cell affects the mass of solid phase present. It is:

$$\frac{dM}{dt} = q C_{in} + r V_t - q C_{eq} \quad (E.1.4)$$

where

M = the mass of solid per unit volume of tailings ($\text{mol}\cdot\text{m}^{-3}$)

For certain ions such as aluminum and iron (III), C_{eq} is a function of pH when the solid phases are basaluminite and iron hydroxide occur in the tailings. This necessitates a mathematical solution of the mass balance for certain ions (e.g. K^+ , Fe^{2+}), a mathematical solution of the electroneutrality equation (E.2.22) to define C_{eq} , and solids mass balance calculations. Thus portions of the mathematical solution for the mass balance, solids mass balance and the electroneutrality equation must be conducted simultaneously or iteratively. For convenience, the algorithm for solution mass balance and solids mass balance is given in the appendix. The algorithm for the electroneutrality equation is given in Appendix F. Required knowledge from either appendix are indicated in the appropriate spot in the verbage.

E.2 Algorithm Development

The mass balance, charge balance and mass transport in the model are

interdependent. For purposes of mathematical solution, however, these can be separated into different components. This section describes the method for quantifying transport of porewater through the tailings assuming plug flow in the unsaturated zone.

The particular calculations employed are a function of the presence or absence of various solids in the system. The two main cases are 1) tailings with calcite and, 2) tailings without calcite. Once the presence (or absence) of calcite has been established the influences of various other solids are examined; gypsum, aluminum solid and iron solid (Figure E.1).

E.2.1 Initial Calculations

The first task is to evaluate all components whose dissolution is not equilibrium controlled. These include minerals such as sericite which contain K^+ and other common ions, silicate minerals, and pyrite oxidation release as Fe^{2+} , Fe^{3+} and SO_4^{2-} . For some of these elements, additional phenomenon such as precipitation into another mineral phase (e.g. SO_4 in gypsum) must subsequently be evaluated. The mass balances on these components are conducted by calculating input from kinetic dissolution and by influx from overlying layers. The relationship for mass balance on potassium gives;

$$K(i,t+1) = K(i-1,t+1) \cdot q(i-1,t+1)/q(i,t+1) + \quad (E.2.2)$$

$$R_{ser}(i) \cdot V_i/q(i,t+1)$$

where

$K(i,t+1)$ = the potassium concentration in box i at the new time ($mol.L^{-1}$)

q = the water flux ($L.mth^{-1}$)

R_{ser} = the dissolution rate of sericite ($mol.m^{-3}.mth^{-1}$)

V_i = the volume of layer i (m^3)



The mass balance on ferrous iron is expressed as:

$$\text{Fe}^{3+}(i,t+1) = \text{Fe}^{3+}(i-1,t+1) \cdot q(i-1,t+1) + X\text{Fe}^{2+}(i) \cdot$$

$$R_{\text{pyr}} \cdot V(i)/q(i,t+1) \quad (\text{E.2.3})$$

where

$X\text{Fe}^{2+}(i)$ = the fraction of pyrite oxidizing to yield Fe^{2+}

R_{pyr} = the rate of pyrite oxidation ($\text{mol} \cdot \text{m}^{-3} \cdot \text{mth}^{-1}$)

The calcium mass balance is given by;

$$\text{Ca}_T(i,t+1) = \text{Ca}_T(i-1,t+1) \cdot q(i-1,t+1)/q(i,t+1) \quad (\text{E.2.4})$$

and for sulfate;

$$\text{SO}_4_T(i,t+1) = \text{SO}_4_T(i-1,t+1) \cdot q(i-1,t+1)/q(i,t+1) +$$

$$X\text{SO}_4 \cdot R_{\text{pyr}}(i) \cdot V(i) / q(i,t+1) \quad (\text{E.2.5})$$

where

$X\text{SO}_4$ = the fraction of pyrite oxidized that yields sulfate

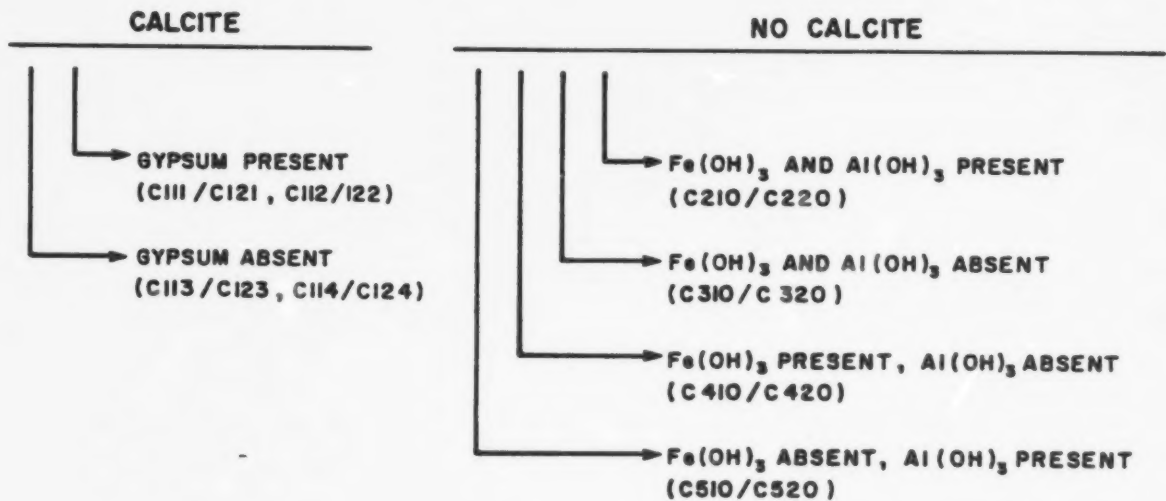
After performing these calculations, the presence of iron and aluminum solids are evaluated and the appropriate computational steps taken. The following sections outline the approach and equations used to calculate mass transport for the various cases with and without particular solids.

For each case, a further distinction is made between open and closed system. Open system refers to calculations performed in the unsaturated zone, which closed system refers to the capillary fringe and saturated zone.

E.2.2 Calcite Present

Once the initial calculations are performed the electroneutrality equation

FIGURE E.1
pH COMPUTATIONAL SCENARIOS



NOTE:

C210/C220 DENOTES CASE 210 (UNSATURATED ZONE)
AND CASE 220 (SATURATED ZONE)

(F.2.22) is solved using the equations presented in Appendix F, Section F.2.2 to calculate pH.

The depletion of calcite is determined from the following expression:

$$\Delta \text{Calcite} = \text{XCT} \cdot R_{\text{pyr}} \cdot dt \quad (\text{E.2.6})$$

where

$\Delta \text{Calcite}$ = depletion of calcite (mol/m^3)

XCT = mass fraction of sulfate from tailings

R_{pyr} = rate of pyrite oxidation ($\text{mol} \cdot \text{m}^{-3} \cdot \text{mth}^{-1}$)

dt = time increment (mth)

However, if the layer above has been depleted of calcite, a second equation is employed which incorporates the acid flux from above:

$$\Delta \text{Calcite} = \text{Xct} \cdot R_{\text{pyr}} \cdot dt - [\text{H}^+] \cdot q \cdot dt/V_t + D_1 + D_2 \quad (\text{E.2.7})$$

where

q = infiltration rate ($\text{L} \cdot \text{mth}^{-1}$)

V_t = volume of layer (m^3)

D_1 = depletion resulting from Al^{3+} ($\text{mol} \cdot \text{m}^{-3}$)

D_2 = depletion resulting from Fe^{3+} ($\text{mol} \cdot \text{m}^{-3}$)

$[\text{H}^+]$ = hydronium concentration ($\text{mol} \cdot \text{L}^{-1}$)

The terms D_1 and D_2 denote the acidity associated with aluminum and iron (III) ions respectively and are defined as:

$$D_1 = \text{AL}^{3+}_{i-1} [\text{CA1OH}_2 \times f_3/f_1 \cdot 10^{2\text{pH}(i-1)} + 2 \cdot \text{CA1OH} \cdot f_3/f_1 \cdot 10^{\text{pH}(i-1)} + 3] \cdot q \cdot dt/V_t \quad (\text{E.2.8})$$

and

$$D_2 = \text{Fe}_{i-1} [\text{CFeOH} \cdot f_3/f_2 \cdot 10^{\text{pH}(i-1)} + 2] \cdot q \cdot dt/V_t$$

E.2.3 Calcite Absent

Case I. Al and Fe(III) Solids Both Present

The charge balance is first used to solve for pH with the appropriate Al^{3+} and Fe^{3+} terms that incorporate solubility constants for the solids. A mass balance calculation is then conducted noting that the Fe^{3+} and Al^{3+} concentrations are fixed by solubility. Therefore, mass balance can be performed on these solids where the equations become;

$$\text{Fe(OH)}_3(\text{s})(i, t+1) = \text{Fe(OH)}_3(\text{s})(i, t) + [q(i-1, t+1) \cdot \text{FeT}(i-1, t)/V(i) - q(i, t+1) \cdot \text{FeT}(i, t)/V(i) + X_{\text{Fe}^{3+}} \cdot R_{\text{pyr}}(i)] \cdot dt(1) \quad (\text{E.2.9})$$

and

$$\text{Al(OH)}_3(\text{s})(t+1, i) = \text{Al(OH)}_3(\text{s})(i, t) + [q(i-1, t+1) (\text{Al}_T)(i-1, t+1)/V(i) - q(i, t+1) \cdot \text{Al}_T / V_i + R_{\text{ser}}] \cdot dt$$

where

- t, i = current timestep and layer, respectively
- $t+1, i-1$ = next time and overlying layer, respectively
- $\text{Fe(OH)}_3(\text{s})$ = ferric hydroxide solid ($\text{mol} \cdot \text{m}^{-3}$)
- $\text{Al(OH)}_3(\text{s})$ = aluminum hydroxide solid ($\text{mol} \cdot \text{m}^{-3}$)
- Fe_T = total ferric solution concentration ($\text{mol} \cdot \text{L}^{-1}$)
- Al_T = total aluminum solution concentration ($\text{mol} \cdot \text{L}^{-1}$)
- $X_{\text{Fe}^{3+}}$ = the stoichiometric fraction of Fe(III) added from pyrite oxidation

The next step involves the precipitation or dissolution of gypsum to equilibrium. During this process, equal masses of Ca^{2+} and SO_4^{2-} are transferred between the liquid and solid phases. In this case, the change in

Ca^{2+} or SO_4^{2-} in solution is calculated as:

$$\Delta \text{SO}_4^{2-} = \Delta \text{Ca}^{2+} = (\text{Ca}^{2+})^*_i - (\text{Ca}^{2+})_i \quad (\text{E.2.10})$$

where the asterisk notation represents the equilibrium value that has been calculated from the solubility product of gypsum.

The equilibrium concentration of Ca^{2+} is determined from the quadratic equation;

$$(\text{Ca}^{2+})_{\text{eq}} = 1/2 (\text{Ca}_t - \text{SO}_4) + (2\text{SO}_4 - 2\text{Ca}_t + 4 (\text{KCaSO}_4/f_2)^2)^{1/2} \cdot S_{\text{fact}} \quad (\text{E.2.11})$$

where Ca_t and SO_4 are the previous total concentration of calcium and sulfate and KCaSO_4 is the association constant for the CaSO_4° complex and S_{fact} is the factor that accounts for all sulfate complexes except CaSO_4° . The new total concentration of Ca^{2+} calculated for gypsum equilibrium is then given by:

$$(\text{Ca}_t)_{\text{eq}} = (\text{Ca}^{2+})_{\text{eq}} (1 + \text{CCaSO}_4 \cdot f_2^2 \cdot (\text{SO}_4)) \quad (\text{E.2.12})$$

For the solid phase;

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})(i, t+1) = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})(i, t) - \text{Delgyp}(i, t+1) \quad (\text{E.2.13})$$

where

$\text{Delgyp}(i, t+1) = (\text{Ca}_t)_{\text{eq}} - (\text{Ca}_t)$; the depletion of gypsum ($\text{mol} \cdot \text{L}^{-1}$)

$(\text{Ca})_{\text{eq}}$ = the total the total expected concentration of (Ca^{2+}) due to equilibrium with gypsum ($\text{mol} \cdot \text{L}^{-1}$)

$(\text{Ca})_t$ = the existing (Ca^{2+}) concentration in cell i ($\text{mol} \cdot \text{L}^{-1}$)

Accounting is also made of the Fe and Al solids so that if these quantities fall below zero during a particular time step, they will be set to zero for the following one.

Case II. Fe and Al Solids are Both Absent

For this condition, the mass balances are performed directly on the dissolved Fe and Al components. The appropriate equations are;

$$(Fe_T)(i,t+1) = (q(i-1,t+1)(Fe_T)(i-1,t+1)) + XFe^{3+} \cdot R_{pyr}(i) \cdot V(i)/q(i,t+1) \quad (E.2.14)$$

and

$$(Al_T)(i,t+1) = (q(i-1,t+1)(Al_T)(i-1,t+1)) + R_{ser} \cdot V(i,t)/q(i,t+1) \quad (E.2.15)$$

The pH is then calculated from the charge balance equation with the appropriate ALUM and IRON3 terms and finally gypsum precipitation or dissolution is conducted in the manner noted above.

Case III. Fe Solid Present Only

In this case, the Al mass balance is performed first as outlined above for soluble Al only. The pH is then calculated from the appropriate electroneutrality equation with the ALUM factor for no solids (equation E.2.15) and the IRON3 factor based on the solubility control. The mass balance on the Fe solid is then performed as in equation (E.2.9) and gypsum dissolution and precipitation is then calculated.

Case IV. Al Solids Present Only

In this case, the mass balance on Fe(III) in solution is calculated from equation (E.2.14) initially. The pH is then derived from the appropriate electroneutrality equation. Mass balance on the Al solid is then performed after which gypsum is dissolved or precipitated.

Calculation Refinement

During the mass transport calculations, it is possible to attain supersaturated conditions with respect to dissolved Fe and Al, after the timestep. This could occur if the pH value changes between timesteps. When this occurs, the assumption about solid phase controlling the pH may be in

this occurs, the assumption about solid phase controlling the pH may be in error. Therefore, further evaluation is needed if super saturation conditions develop.

If it is assumed that either solid is absent, saturation conditions for that solid in solution are evaluated after pH and mass balance calculations are completed. If supersaturation has occurred between time steps, then the amount of aluminum solid which will precipitate is calculated from:

$$\text{Al(OH)}_3(s)(i,t+1) = (\text{Al}_T)_*(i,t+1) - (\text{Al}_T)(i,t) \quad (\text{E.2.16})$$

where the asterisk notation indicates the equilibrium total dissolved concentration. The total dissolved Al in that layer is then set to the equilibrium value. Precipitation of the solid will cause a small shift in calculated pH, and suggest the need to further iterate toward the precise solution. It is possible that several iterations are needed to calculate equilibrium values for pH and total dissolved Al and Fe concentrations. These iterations were not performed because an evaluation during the model runs showed that these adjustments did not represent large errors in calculating pH and mass balance.

E.2.4 Other Solids

The remaining solids, including pyrite and sericite, require mass balances to track their presence in the tailings profile. The equations for these solids are;

$$\text{Sericite}(i,t+1) = \text{Sericite}(i,t) - R_{\text{ser}}(i) \cdot dt \quad (\text{E.2.17})$$

and

$$\text{Pyrite}(i,t+1) = \text{Pyrite}(i,t) - R_{\text{pyr}}(i) \cdot dt \quad (\text{E.2.18})$$

The terms R_{ser} and R_{pyr} are the dissolution rates of sericite and pyrite

respectively.

E.3 Parameter Distributions

The following section discusses the parameters employed in the transport module. Also presented are the parameter probability distributions types, descriptions and the computer source symbols (Table E.3.1).

E.3.1 Infiltration Rate and Flow

The infiltration rate, V_r , is the velocity (m/month) at which water infiltrates the tailings assuming steady state conditions exist. Table E.3.1 lists the infiltration rates as a function of month. The infiltration rates through different layers was assumed to be the same in a particular month. The allocation of flow among the various months is based upon longterm average rainfall corrected for infiltration of melting snow in the spring from snow which accumulates over the winter period.

The infiltrating flow is defined as the volumetric throughput of water through the tailings and is calculated from:

$$q = V_r \cdot A_x \cdot 1000 \quad (E.3.1)$$

where

q = infiltrating flow (L.mth₋₁)

A_x = cross sectional area of tailings (m₂)

The constant, 1000, converts the flow from units of metres cubed to litres. The latter being required in the speciation module.

E.4 Sensitivity/Uncertainty Analyses

Because of the interdependency of the two modules, a joint sensitivity/uncertainty analyses was performed in Appendix F, section 5.0, for the solute transport and aqueous speciation modules.

Table E.3.1

SOLUTE TRANSPORT MODULE PARAMETERS

Symbol	Description	Units	Nominal	Probabilistic	Origin	Code
A_x	cross-sectional area of the tailings	(m ²)	3.0×10^7	$C(3.0 \times 10^7)$	Input	ATAIL
CO_2	carbon dioxide concentrations	(mol.L ⁻¹)	calculated	calculated	Transport	CO2
q	infiltration rate	(L.mth ⁻¹)	calculated	calculated	Initial	VRIN(i,M)
R_{pyr}	rate of pyrite oxidation	(mol.m ⁻³ .mth ⁻¹)	calculated	calculated	Pyrite	RPYR(i)
V	infiltration rate for each month (i.e. for January, m=1; June, m=6)	(m.mth ⁻¹)	m=1 0.005 2 0.005 3 0.005 4 0.090 5 0.070 6 0.030 7 0.020 8 0.030 9 0.050 10 0.050 11 0.040 12 0.005	T(0.001,0.005,0.01) T(0.001,0.005,0.01) T(0.001,0.005,0.01) T(0.018,0.09,0.18) T(0.014,0.07,0.14) T(0.006,0.03,0.06) T(0.004,0.02,0.04) T(0.006,0.03,0.06) T(0.01,0.05,0.1) T(0.01,0.05,0.1) T(0.008,0.04,0.08) T(0.001,0.005,0.01)	Input	VR(i,m)
V_t	volume of a layer	(M ³)		calculated	calculated	VT(i)

Key to Probabilistic:

Parameters Value: C - Constant (single value)
T - Triangular (min., mode, max.)

Note

m - month of the year
i - layer

APPENDIX F: AQUEOUS SPECIATION MODULE (MODULE VI)

F.1 Theoretical Background

The objective of the aqueous speciation module is to calculate the pH of the solution for a given solution composition. This calculation is based upon the electroneutrality equation which is derived from the principle of charge balance. This principle basically states that a solution must be electrically neutral and hence that the sum of positive charges in solution must equal the sum of negative charges in solution.

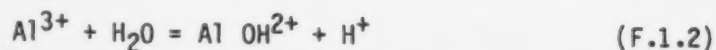
For ions present in leachate from the uranium mill tailings, the following is the electroneutrality equation:

$$\begin{aligned} & [H^+] + 2[Ca]^{2+} + 3[Fe^{3+}] + 2[FeOH^{2+}] + [Fe(OH)_2^+] + [FeSO_4^+] + 2[Fe^{2+}] \\ & + 3[Al^{3+}] + 2[AlOH^{2+}] + [Al(OH)_2^+] + [AlSO_4^+] + [K^+] \\ & = [HCO_3^-] + 2[CO_3^{2-}] + 2[SO_4^{2-}] + [Fe(OH)_4^-] + [Al(OH)_4^-] + [NO_3^-] \end{aligned} \quad (F.1.1)$$

Here [ions] represents the concentrations of these ions in solution. By balancing the concentrations of all other ions in solution, the H^+ concentration and hence the pH can be calculated directly.

However, the problem is complicated by the different procedures required to estimate the concentration of the other cations and anions. First various ions are themselves a function of the pH.

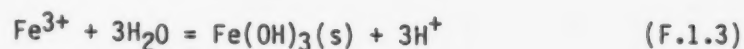
Iron (III) and aluminum hydrolyze to form various hydrolytic complexes. For example, the reaction:



describes the hydrolyses of Al^{3+} to form $AlOH^{2+}$ and H^+ . Second, various ions may be estimated from solution mass balance principles (e.g. potassium) while



others (e.g. Al^{3+} , Fe^{3+} , Ca^{2+}) may be estimated from equilibrium principles. Ions are estimated from equilibrium principles if a solid phase is present, which contains the ion and which is at equilibrium with the solution phase. If the solid phase completely dissolves, the solution mass balance is used to estimate the ion concentration. The equilibrium solution concentrations are a function of pH for various ions (e.g. aluminum and iron). For example, [iron] is a function of pH according to:



Hence to estimate pH, the overall electroneutrality equation must be phrased as a function of pH and appropriate total solution concentrations or solid phases, and then solved mathematically for pH. This requires that an iterative solution be used to solve the basic equation.

In this section, the algorithm for solving the basic electroneutrality equation, and for estimating solution concentrations of elements such as aluminum and iron at equilibrium with solid phases are given. In particular, simplifications are available which facilitate the mathematical solution.

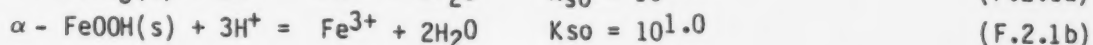
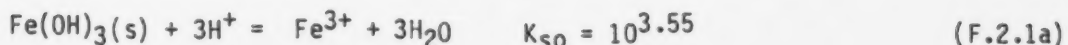
F.2 Algorithm Development

A complex chemical equilibria problem is posed by the large number of solids and dissolved species, including hydrolysis products, in the tailings. Hence, simplification of the problem was required to reduce the computation time of the mathematical solution. Wherever possible, therefore, the chemical model has been reduced to compartments in which only those parts of the whole which contribute significantly to the electroneutrality equation are used. For instance, components that contribute only slightly to the overall charge balance and hence to the determination of pH are not considered. But, carefull consideration is given to the various components, whose importance may change with pH itself or with other conditions.

F.2.1 Relative Importance of Al and Fe to the Electroneutrality Equation in pH 6-8 Range

This section discusses the importance of Al^{3+} and Fe^{3+} near neutral pH and shows why many terms in the electroneutrality equation can be ignored in the calculation of pH. In later sections, various subsets of the electroneutrality equation are presented which allow simplification of the mathematical problem of solving the electroneutrality equation for pH. The conditions under which the simplification applies and the mathematical formulation are also given.

The importance of iron and aluminum at neutral pH can be determined by inspection of their equilibrium relationships. For iron solubility, there are two extreme states defined by:



The $\alpha - \text{FeOOH}(\text{s})$ is the more stable form. The speciation of iron is given in Figure F.1; for $\alpha - \text{FeOOH}(\text{s})$, indicating that the minimum solubility is of the order of 10^{-11} M for total aqueous iron (Fe_T). If the more amorphous form is present, then the solubility is increased by approximately two orders of magnitude; of the order of 10^{-9} M for Fe_T .

A speciation diagram for aluminum is given in Figure F.2 assuming that basaluminite or amorphous $\text{Al(OH)}_3(\text{s})$ is present as the solid phase. The diagram indicates a minimum solubility of approximately $10^{-4.5}$ M for Al_T .

For other ions in the electroneutrality equation such as calcium and sulfate, their concentration is controlled by gypsum equilibrium when the solid phase is present. For equimolar concentrations, the equilibrium concentration is $10^{-2.3}$ molar. These concentrations are an order of magnitude or more higher than that of aluminum and iron. Accordingly at neutral pH, the aqueous

concentrations of aluminum and iron can be negligible because they have a very small effect on the electroneutrality equation in comparison to calcium and sulfate. Similar analysis for the effects of many ions can also be made. In this section, an analysis of solution conditions is now made in which calcite is present and controls the porewater pH to determine under which conditions aluminum, iron and other ions make a negligible contribution to the electroneutrality equation. The analysis starts by assuming that calcium concentrations are at equilibrium with both calcite and gypsum.

For the simultaneous equilibrium between porewater and two solid phases, calcite and gypsum, the equations are:

$$\text{Gypsum Solubility: } A_{\text{Ca}} \cdot A_{\text{SO}_4} = K_{\text{CaSO}_4} \quad (\text{F.2.2a})$$

$$\text{Calcite Solubility: } A_{\text{Ca}} \cdot A_{\text{CO}_3} = K_{\text{CaCO}_3} \quad (\text{F.2.2b})$$

$$\text{Electroneutrality: } 2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + 2[\text{SO}_4^{2-}] \quad (\text{F.2.2c})$$

Inorganic Carbon

$$\text{Speciation: } \frac{A_{\text{HCO}_3} \cdot A_{\text{H}}}{A_{\text{H}_2\text{CO}_3^*}} = K_1 \quad (\text{F.2.2d})$$

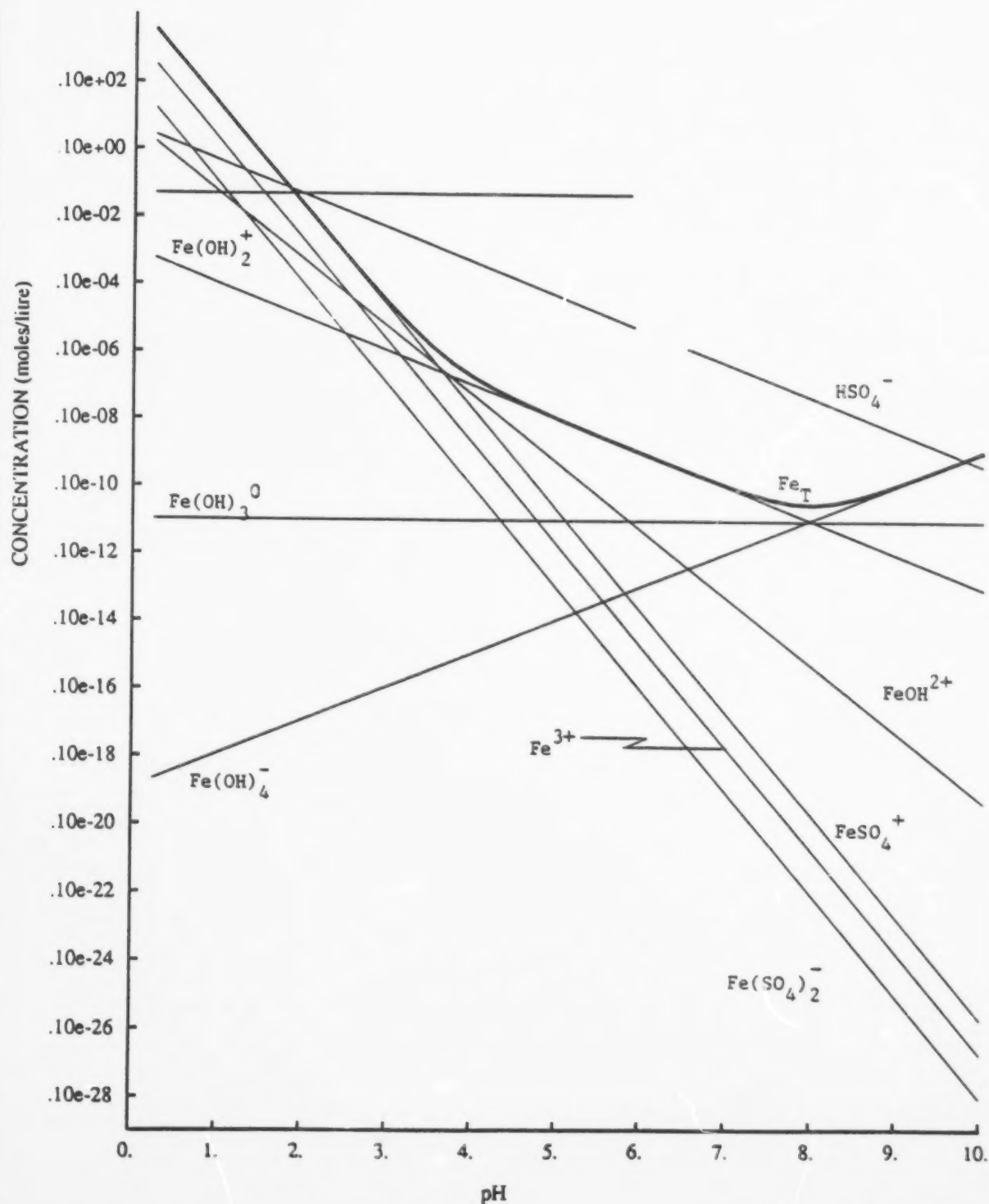
$$\frac{A_{\text{H}} \cdot A_{\text{CO}_3}}{A_{\text{HCO}_3}} = K_2 \quad (\text{F.2.2e})$$

$$\text{Carbon Mass Balance: } C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{F.2.2f})$$

$$\text{Henry's Law: } [\text{H}_2\text{CO}_3^*] = K_H \cdot p_{\text{CO}_2} \quad (\text{F.2.2g})$$

When the layer is saturated (i.e., a closed system to CO_2), C_T is set by solution mass balance. When the layer is unsaturated, C_T is set by p_{CO_2} and by pH.

FIGURE F.1
CONCENTRATION vs. pH
FOR Fe(III) TOTAL



Assuming Henry's Law is used to set $H_2CO_3^*$ as a function of pCO_2 , simplification of these equations for the neutral pH range results in two equations:

$$[Ca^{2+}]^2 = \frac{H^+ K_{CaCO_3}}{K_2 f[Ca^{2+}] f_{HCO_3}} + \frac{f_{Ca}}{f_{SO_4}} K_{CaSO_4} \quad (F.2.3a)$$

$$[Ca^{2+}] = \frac{(H^+)^2 K_{CaCO_3}}{K_1 K_2 K_{H^+} pCO_2} \quad (F.2.3b)$$

where f = an activity coefficient.

Substitution of H^+ from (F.2.3b) and (F.2.3a) gives:

$$(Ca^{2+})^2 - \frac{f_{Ca}}{2f_{HCO_3}} \frac{K_1 K_H K_{CaCO_3} [Ca^{2+}]^{1/2}}{K_2 pCO_2} - \frac{f_{Ca}}{f_{SO_4}} K_{CaSO_4} = 0 \quad (F.2.4)$$

This is a fourth order polynomial for which there is not an analytical solution available. However, an analytical solution can be obtained if it can be further simplified. Inspection of the equation shows the second term is due to calcium equilibrium with calcite while the third term is due to calcium equilibrium with gypsum.

The intersection of equation (F.2.3a) and equation (F.2.3b) on a plot of Ca^{2+} vs pH defines the root of equation (F.2.4).

These equations are plotted on Figure F.3 for a range of pCO_2 values, from $10^{-1.5}$ atm to $10^{-3.5}$ atm. The intersection of equation (F.2.3b) with (F.2.3a) indicates that the first term on the right hand side of equation (F.2.3a) does not significantly influence the value of the equation in the range of the root of equation (F.2.4). Accordingly, the first term on the right hand side of equation (F.2.3a) may be ignored in the pH range of interest here. This

results in the following equations for the open system:

$$[\text{Ca}^{2+}] = \left[\frac{\text{KCaSO}_4}{f_{\text{Ca}} f_{\text{SO}_4}} \right]^{1/2} \quad (\text{F.2.5a})$$

$$[\text{H}^+] = \left[\frac{\text{K}_1 \text{K}_2}{\text{KCaCO}_3} \frac{\text{K}_\text{H} \text{pCO}_2 f_{\text{Ca}} [\text{Ca}^{2+}]}{1} \right]^{1/2} \quad (\text{F.2.5b})$$

$$[\text{SO}_4^{2-}] = [\text{Ca}^{2+}] \quad (\text{F.2.5c})$$

$$\text{C}_\text{T} = \text{PCO}_2 \cdot \text{K}_\text{H} \left[\frac{[\text{H}^+] + \text{K}_1}{[\text{H}^+]} \right] \quad (\text{F.2.5d})$$

$$[\text{HCO}_3^-] = \left[\frac{\text{K}_1}{[\text{H}^+] + \text{K}_1} \right] \text{C}_\text{T} \quad (\text{F.2.5e})$$

Conceptually, these results seem to be in disagreement with the role of extra sulphate from pyrite dissolution. For example, consider a mass balance on an intermediate layer (e.g., layer 2) in which $[\text{Ca}^{2+}] = (\text{SO}_4^{2-})$ in the layer 1) due to the depletion of pyrite. Thus gypsum dissolution in layers above sets the ratio of (Ca^{2+}) to (SO_4^{2-}) entering the intermediate layer. Pyrite dissolution in Layer 2 may increase sulphate up to ten times for example, altering the original Ca:SO₄ ratio. However, the acid produced attacks calcite and liberates calcium from calcite. The overall reaction involving pyrite oxidation and gypsum dissolution can be represented by:

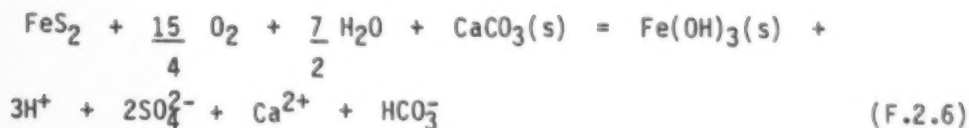


FIGURE F.2
CONCENTRATION vs. pH FOR AL(III) TOTAL
BASED ON BASALUMINITE SOLID

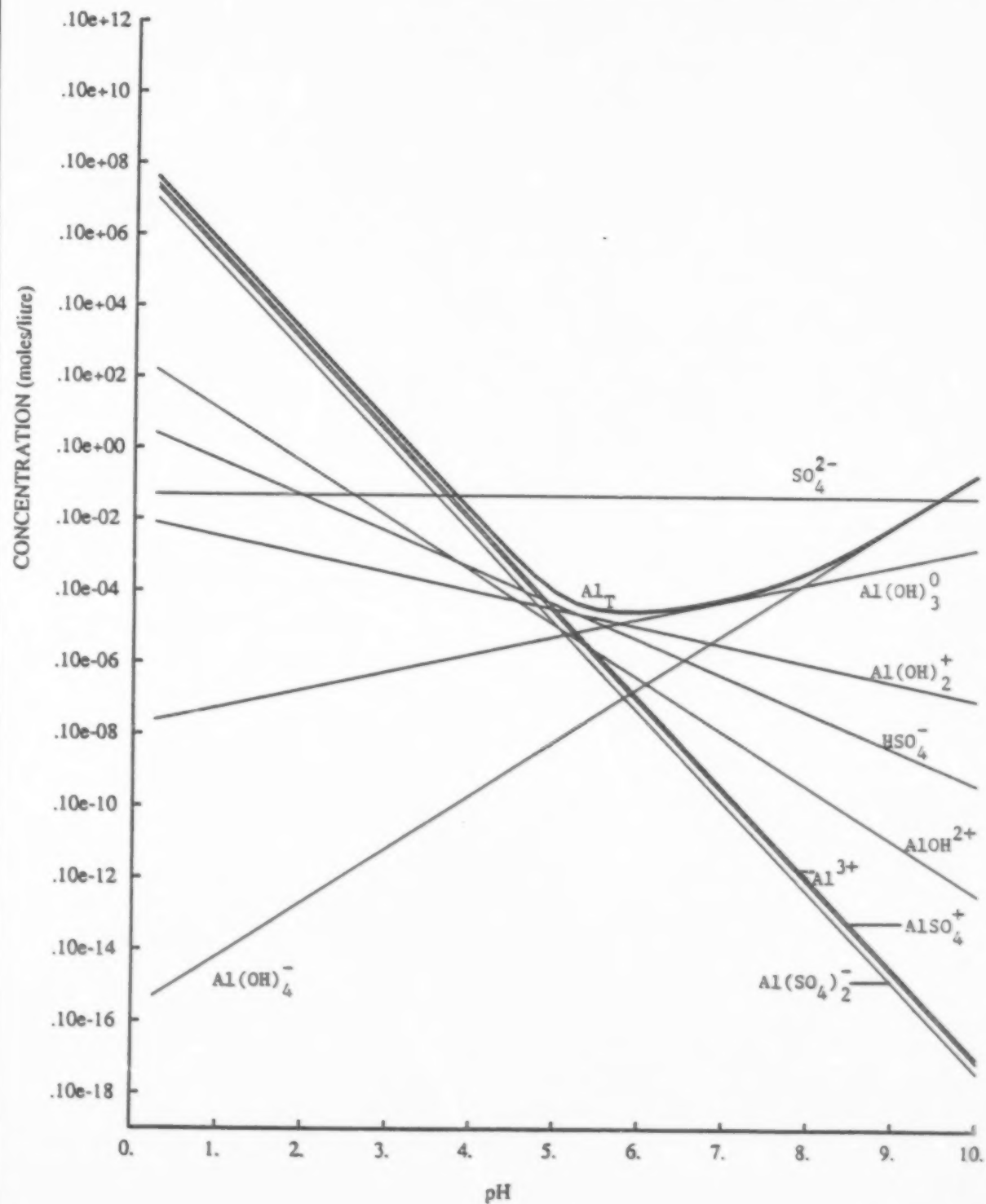
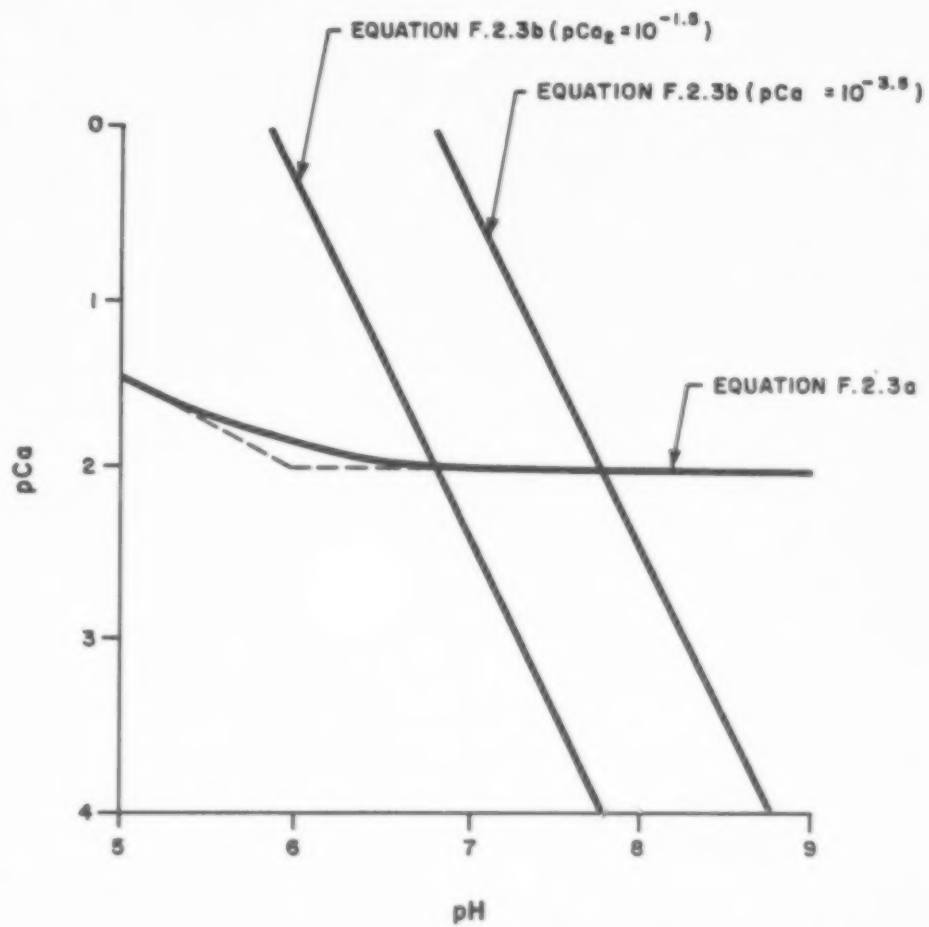
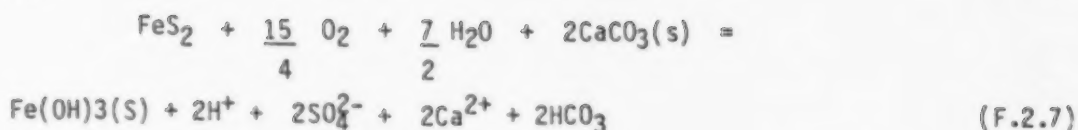


FIGURE F.3
ROOTS OF pH DETERMINING EQUATION



or



Accordingly, the liberation of Ca from calcite can be balanced by the liberation of sulphate from pyrite.

Evaluation of equation (F.2.5a) shows that activity coefficients for f_{Ca} and f_{SO_4} are of the order of 0.5 and the value for the KCaSO_4 is $10^{-4.61}$; the equilibrium Ca^{2+} and SO_4^{2-} concentrations are of the order of $10^{-2.3}$ M or (400 mg/L Ca^{2+} and SO_4^{2-} is 960 mg/L). The total dissolved concentration is greater than that of the two ions singly due to formation of the CaSO_4 complex.

To ascertain the importance of aluminum, and other ions, consider the following overall electroneutrality equation:

$$\begin{aligned} & [\text{H}^+] + 2[\text{Ca}^{2+}] + 3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{FeSO}_4] + 2[\text{Fe}^{2+}] \\ & 3[\text{Al}^{3+}] + 2[\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{AlSO}_4] = [\text{HCO}_3] + \\ & 2[\text{CO}_3^{2-}] + 2[\text{SO}_4^{2-}] + [\text{Fe}(\text{OH})_4^-] + [\text{Al}(\text{OH})_4^-] \end{aligned} \quad (\text{F.2.8})$$

The terms involving iron species are all of the order of 10^{-8} M or less in magnitude (see Figure F.1). The terms involving aluminum are of the order of $10^{-4.5}$ M or less in magnitude (see Figure F.2). For $\text{Ca}^{2+} = 10^{-2}$ M and considering overall calcite equilibrium equation of:

$$\text{H}^+ = \frac{\text{K}_1 \text{K}_2 \text{K}_\text{H} \text{PCO}_2 f_{\text{Ca}}}{\text{KCaCO}_3} \cdot [\text{Ca}^{2+}]^{0.5} \quad (\text{F.2.9})$$

$$= \frac{10^{6.3} 10^{-10.3} 10^{-5} (0.5)[\text{Ca}^{2+}]^{0.5}}{10^{-8.3}} \quad (\text{F.2.10})$$

$$= (10^{-13.6} [\text{Ca}^{2+}])^{0.5}$$

the equilibrium pH is 5.8. Accordingly the terms involving H^+ and CO_3^{2-} are less than $10^{-6}M$ and hence negligible. Thus, the only terms of significance are those for calcium, sulphate and bicarbonate, giving the effective electroneutrality equation as:

$$2Ca^{2+} = HCO_3^- + 2SO_4^{2-} \quad (F.2.11)$$

That is the electroneutrality equation does not need to consider Fe^{3+} or Al^{3+} species at neutral pH when both calcite and gypsum are present.

In the anoxic zone, the same argument applies except that Fe^{2+} may become a significant part of the electroneutrality equation. Fe^{2+} does not hydrolyze significantly until $pH = 9$ (see Figure F.4). Accordingly, the electroneutrality equation is defined by

$$2Ca^{2+} + 2Fe^{2+} = HCO_3^- + 2SO_4^{2-} \quad (F.2.12)$$

If Fe^{2+} is small in the electroneutrality equation (e.g., less than $10^{-3}M$), equation (F.2.2g) results in the following quadratic equation

$$[Ca^{2+}]^2 - \frac{f_{Ca}}{2} \cdot C_T [Ca^{2+}] - \frac{f_{Ca}}{f_{SO4}} \cdot KCaSO_4 = 0 \quad (F.2.13a)$$

where solution is:

$$[Ca^{2+}] = 1/2 (C_1 + (C_2 + 4C_2)^{0.5}) \quad (F.2.13b)$$

in which;

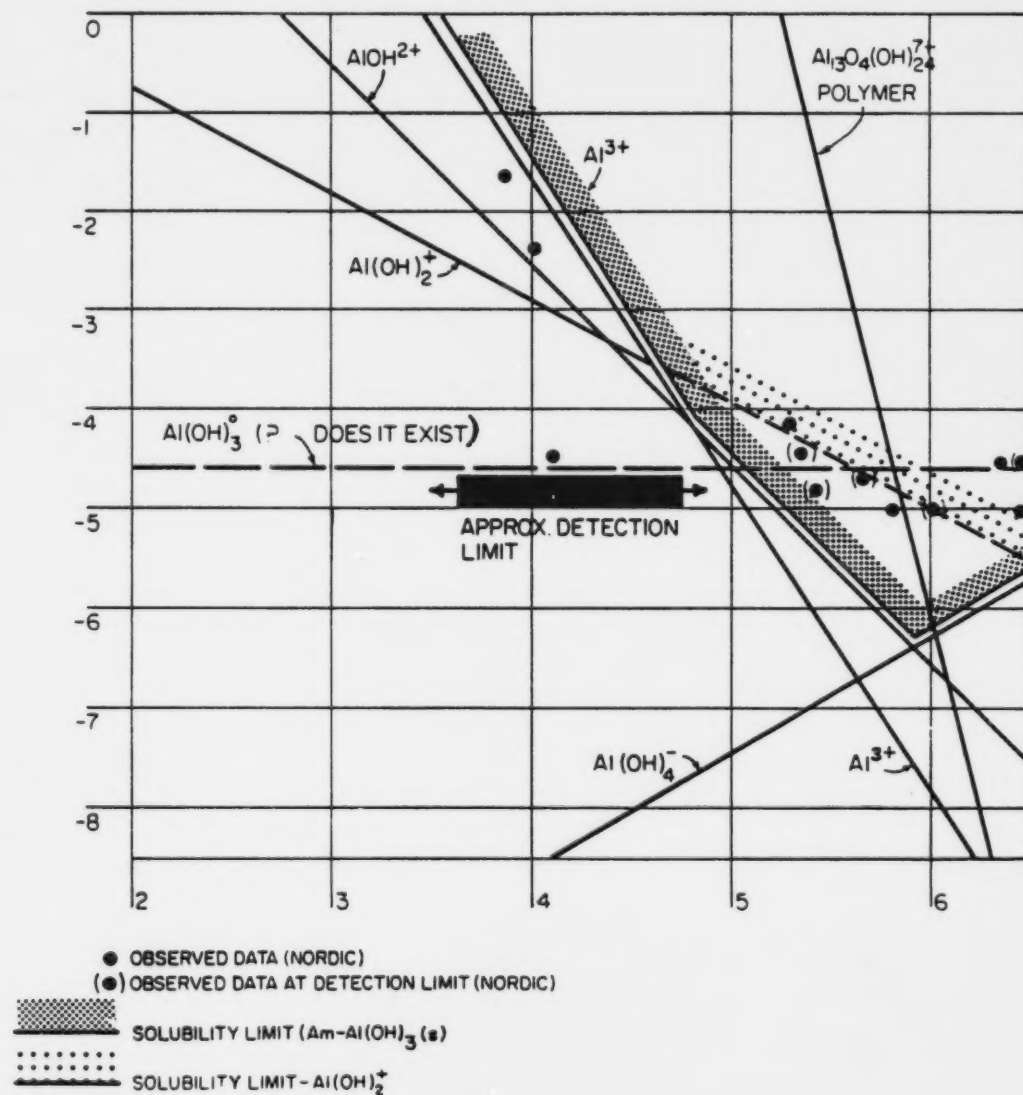
$$C_T = \text{calculated by solution mass balance} \quad (F.2.13c)$$

$$C_1 = C_T/2 \quad (F.2.13d)$$

$$C_2 = \frac{KCaSO_4}{f_{Ca} f_{SO4}} \quad (F.2.13e)$$

FIGURE F.4

**SPECIATION DIAGRAM FOR ALUMINUM
(AMORPHOUS $\text{Al}(\text{OH})_3$ (s);
DATA FROM BAES AND MESMER, 1976)**



Reference Adapted from BEAK, 1985



$$(\text{SO}_4^{2-}) = C_2 / [\text{Ca}^{2+}] \quad (\text{F.2.13f})$$

$$(\text{HCO}_3^-) = C_T \quad (\text{F.2.13g})$$

$$\text{H}^+ = \frac{f_{\text{Ca}} [\text{Ca}^{2+}] \cdot f_{\text{HCO}_3} (\text{HCO}_3^-) \cdot K_2}{K_{\text{CaCO}_3}} \quad (\text{F.2.13h})$$

Here again, the terms for calcium and sulphate are large meaning that Iron (III) and Aluminum (III) species are negligible.

For conditions where Fe^{2+} are significant, its contribution to electroneutrality may be calculated by mass balance, or by equilibrium with siderite if siderite is present. For siderite equilibrium, the following equations:

$$2\text{Ca}^{2+} + 2\text{Fe}^{2+} = \text{HCO}_3^- + 2\text{SO}_4^{2-} \quad (\text{F.2.14})$$

$$f_{\text{Fe}} f_{\text{CO}_3} \cdot [\text{Fe}^{2+}] [\text{CO}_3^{2-}] = K_{\text{FeCO}_3} \quad (\text{F.2.15})$$

result in a slightly different second order quadratic:

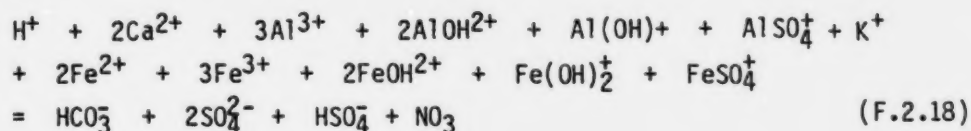
$$[\text{Ca}^{2+}]^2 - \frac{f_{\text{Ca}} C_T (\text{Ca}^{2+})}{A_1} - \frac{2 K_{\text{CaSO}_4}}{A_1 f_{\text{Ca}} f_{\text{SO}_4}} = 0 \quad (\text{F.2.16})$$

$$\text{where } A_1 = 2 + 2 \frac{K_{\text{FeCO}_3}}{K_{\text{CaCO}_3}} \quad (\text{F.2.17})$$

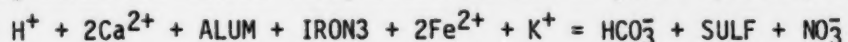
F.2.2 Calculation of pH and Chemical Speciation and pH Evaluation

Solving for pH requires the use of the electroneutrality equation. Solving for the various terms in the equations relating to ferric iron and aluminum species will require knowledge of whether or not solid phases are present to control solubility and whether or not calcite is present. Different methods of solution are required if these solids are not present or have been depleted in the tailings. The various cases that can occur in the evaluation of acidic tailings are presented here with the mathematical approach used to solve for pH. Because sulfate and ferrous iron are added to solution during pyrite oxidation and because Ca^{2+} is affected by gypsum dissolution or precipitation, these constituents are determined by appropriate mass balance calculations. Other ions that are not controlled by equilibrium (e.g., K^+ from sericite dissolution) are also determined from mass balance considerations.

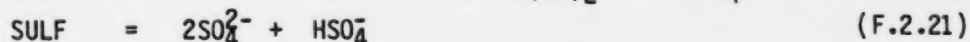
The electroneutrality equation is:



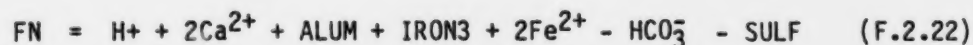
Reassigning terms for ferric iron, aluminium and sulphate species, results in:



where



Collecting all terms to the right hand side results in the definition of a function (FN) as:



FN must be equal to zero to achieve a mathematical solution. The pH where $\text{FN}=0$ is the solution pH.

The next step requires that all terms, not pre-defined or found by independent mass balance, be expressed in terms of pH. The following sections illustrate the approach to establishing and solving the charge balance equation to calculate the solution pH.

Aluminum Chemistry

A mass balance on aluminum species in solution gives;

$$Al_T = Al^{3+} + AlOH^{2+} + Al(OH)_2^+ + Al(OH)_3^0 + AlSO_4^+ \quad (F.2.23)$$

Equilibrium speciation of aluminum can be represented by the following reactions;



The mass action equations corresponding to these reactions are;

$$\frac{f_2 [AlOH^{2+}][H^+]}{f_3 [Al^{3+}]} = K_{ALOH} \quad (F.2.28)$$

$$\frac{f_1 [AlOH_2^+][H^+]^2}{f_3 [Al^{3+}]} = K_{ALOH2} \quad (F.2.29)$$

$$\frac{[Al(OH)_3^0][H^+]^3}{f_3 [Al^{3+}]} = K_{ALOH3} \quad (F.2.30)$$

$$\frac{f_1 [\text{AlSO}_4^+]}{f_3 f_3 [\text{Al}^{3+}][\text{SO}_4^{2-}]} = \text{CALSO}_4 \quad (\text{F.2.31})$$

where the symbols on the right hand side of the equations represent the thermodynamic stability constants for reactions (F.2.24) to (F.2.27) respectively, and f terms are the activity coefficients for ions with the value of the absolute charge as the subscript. Round brackets are concentrations. Then the mass balance on Al in solution becomes;

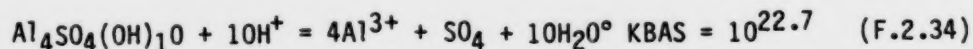
$$\text{Al}_T = [\text{Al}^{3+}] \cdot \text{ALFACT} \quad (\text{F.2.32})$$

$$\begin{aligned} \text{where ALFACT} = & \frac{\text{CALOH} \cdot f_3}{(\text{H}^+) \cdot f_2} + \frac{\text{CALOH}_2 \cdot f_3}{f_1 \cdot (\text{H}^+)^2} + \frac{\text{CALOH}_3 \cdot f_3}{(\text{H}^+)^3} \\ & + \text{CALSO}_4 \cdot \frac{f_3 f_2 (\text{SO}_4)}{f_1} \end{aligned} \quad (\text{F.2.33})$$

The mathematical formulation for ALUM in equation F.2.22 depends upon whether aluminum solid is present or is not present to control solubility. Its formulation is now evaluated for two cases: (i) aluminum solid present and (ii) aluminum solid absent.

Aluminum Solid Present (Basaluminite)

The dissolution reaction for basaluminite is;



The basaluminite mass action equation is given by;

$$[Al^{3+}] = \left(\frac{[H^+]^{10} \text{KBAS}}{[SO_4^{2-}] f_2} \right)^{0.25 / f_3} \quad (\text{F.2.35})$$

where KBAS is the solubility constant. Then (ALUM) is defined as:

$$\text{ALUM} = [Al^{3+}] \left[3 + \frac{2\text{CALOH} \cdot f_3}{[H^+] f_2} + \frac{\text{CALOH2} \cdot f_3}{f_1 [H^+]^2} + \frac{\text{CALOH3} \cdot f_3}{(H^+)^3} + \frac{\text{CALS04} \cdot f_2 f_3 [SO_4^{2-}]}{f_1} \right] \quad (\text{F.2.36})$$

where Al^{3+} is defined by the right hand side of equation F.2.35. However, ALUM is defined completely in terms of H^+ (or pH), and SO_4^{2-} which is determined from mass balance. In summary, the aluminum species in the charge balance can be summarized as;

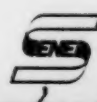
$$\text{ALUM} = \text{ALITY} [Al^{3+}] \quad (\text{F.2.37})$$

$$\text{ALITY} = \left[3 + 2 \frac{\text{CALOH} f_3 10^{\text{pH}}}{f_2} + \frac{\text{CALOH2}}{f} \cdot f_3 + \text{CALOH3} \cdot f_3 \cdot 10^{3\text{pH}} + \frac{\text{CALS04} \cdot f_2 f_3}{f_1} [SO_4^{2-}] \right]$$

Aluminum Solid Not Present

When the aluminum solid has completely dissolved, the mass balance for soluble species Al_T applies. Al^{3+} is defined by:

$$Al^{3+} = Al_T / \text{ALFACT} \quad (\text{F.2.38})$$



where

$$\begin{aligned} \text{ALFACT} = & 1 + \text{CALOH} \frac{f_3}{f_2} 10^{\text{pH}} + \text{CALOH}_2 \frac{f_3}{f_1} 10^{2\text{pH}} + \text{CALOH}_3 \frac{f_3}{f_0} 10^{3\text{pH}} \\ & + \text{CALS04} \frac{f_3 f_2}{f_1} [\text{SO}_4^{2-}] \end{aligned}$$

and the total Al concentration $[\text{Al}_T]$ is known by accounting for inputs, outputs and dissolution of Al from non-equilibrium solids.

Therefore, the charge balance contribution for aluminum is expressed as;

$$\text{ALUM} = \text{ALITY} \cdot \text{Al}_T / \text{ALFACT} \quad (\text{F.2.39})$$

The contribution of Al species in the charge balance is known and is expressed in terms of pH and other known quantities.

Ferric Iron Chemistry

The chemistry of ferric iron in solution is completely analogous to that of aluminum. The total Fe(III) concentration in solution FE^3_T is given by;

$$\text{FE}^3_T = \text{Fe}^{3+} + \text{FeOH}^{2+} + \text{Fe}(\text{OH})_2^+ + \text{Fe}(\text{OH})_3^0 + \text{FeSO}_4^+ \quad (\text{F.2.40})$$

Consideration of ferric iron complexation gives:

$$\text{FE}^3_T = [\text{Fe}^{3+}] \cdot \text{FEFACT} \quad (\text{F.2.41})$$

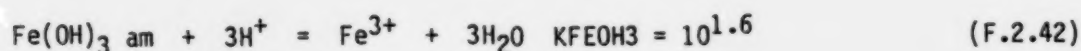
where;

$$\begin{aligned} \text{FEFACT} = & 1 + \frac{\text{CFE0H} \cdot f_3}{(\text{H}^+) \cdot f_2} + \frac{\text{CFE0H}_2 \cdot f_3}{(\text{H}^+)^2 \cdot f_1} + \frac{\text{CFE0H}_3 \cdot f_3}{[\text{H}^+]^3} + \\ & \frac{\text{CFES0H} \cdot f_3 f_2 [\text{SO}_4^{2-}]}{f_1} \end{aligned}$$

The contribution of iron to the charge balance equation is dependent upon the presence or absence of an iron solid. Its evaluation leads to two possible uses (i) Fe(OH)_3 Present, and (ii) Fe(OH)_3 Absent.

Ferric Iron Solid Present (Fe(OH)_3 amorphous)

The solubility of Fe(OH)_3 (am) is given by the reaction;



Its mass action equation in terms of Fe^{3+} is;

$$[\text{Fe}^{3+}] = K_{\text{FeOH3}} \cdot (\text{H}^+)^3 / f_3 \quad (\text{F.2.43})$$

The contribution of ferric iron to the charge balance is then;

$$\text{IRON3} = \text{FEITY} \cdot (\text{Fe}^{3+}) \quad (\text{F.2.44})$$

where;

$$\begin{aligned} \text{FEITY} = 3 + & \frac{2\text{CFE0H} \cdot f_3 \cdot 10^{\text{pH}}}{f_2} + \frac{\text{CFE0H2} \cdot f_3 \cdot 10^{2\text{pH}}}{f_1} + \\ & \frac{\text{CFE0H3} \cdot f_3 \cdot 10^{3\text{pH}}}{f_1} + \frac{\text{CFES0H} \cdot f_3 f_2 [\text{SO}_4^{2-}]}{f_1} \end{aligned} \quad (\text{F.2.45})$$

The contribution to the charge balance (IRON3) is then a function of the solubility for Fe^{3+} (Equation F.2.43), pH, and known complexation constants.

Ferric Iron Solid Not Present

Again by analogy;

$$\text{IRON3} = \text{FEITY} \cdot \text{Fe}_3\text{T}/\text{FEFACT}$$

Therefore, when the total ferric iron concentration is accounted for by mass balance calculations, the contribution to the charge balance is known.

Sulfate Chemistry

The ferric iron and aluminum solution chemistry is dependent on sulfate concentrations. Because the pH can be in the range below a value of 2, the complex HSO_4^- must also be accounted for. The mass balance for dissolved sulfate is given by;

$$S_T = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{AlSO}_4] + [\text{FeSO}_4] \quad (\text{F.2.46})$$

The sulfate protonation reaction is given by:

$$[\text{HSO}_4^-] = [\text{H}^+] + -[\text{SO}_4^{2-}] \quad \text{CHSO}_4 = 10^{-1.9} \quad (\text{F.2.47})$$

for which the complexation equation is;

$$\frac{(\text{H}^+) \cdot f_2 (\text{SO}_4^{2-})}{f_1 (\text{HSO}_4^-)} = \text{CHSO}_4 \quad (\text{F.2.48})$$

Therefore, total dissolved sulfate is given by;

$$S_T = [\text{SO}_4^{2-}] \left(1 + \frac{[\text{H}^+] \cdot f_2}{\text{CHSO}_4 \cdot f_1} + \text{CALSO}_4 \cdot \frac{f_3 f_2}{f_1} \cdot [\text{Al}^{3+}] \right)$$

$$+ \text{CFES04} \cdot \frac{f_3 f_2}{f_1} [\text{Fe}^{3+}] \quad (\text{F.2.49})$$

or;

$$S_T = \text{SFACT} \text{SO}_4^{2-}$$

$$\text{where } \text{SFACT} = 1 + \frac{10^{-\text{pH}} f_2}{f_1 \text{CHS04}} + \text{CALS04} \frac{f_3}{f_1} f_2 [\text{Al}^{3+}]$$

$$\text{CFES04} \frac{f_3 \cdot f_2}{f_2} [\text{Fe}^{3+}]$$

The Al^{3+} and Fe^{3+} terms are defined by the appropriate relationships depending upon whether iron and aluminum solids are present or not.

Carbonate Chemistry

The case in which calcite (CaCO_3) is present was discussed previously. This section deals with the relationships describing carbonate equilibria in the absence of calcite. Two possible situations can occur. The first will apply to the vadose zone where CO_2 gas can exsolve to the gas phase in the tailings pore spaces. This is considered to be an open system where the partial pressure of CO_2 remains constant. Below the water table CO_2 cannot exsolve and total carbonate is conserved. This is a closed system.

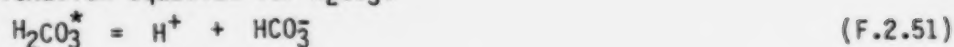
Closed System

In this case, total carbonate (C_T) is constant and is determined by solution mass balance. It is assumed that the pH remains below a value of 9. Therefore;



$$C_T = H_2CO_3^* + HCO_3^- \quad (F.2.50)$$

The complexation equation for $H_2CO_3^*$,



has a mass action equation of:

$$\frac{[H^+][HCO_3^-]}{H_2CO_3^*} f_1 = K_1 \quad (F.2.52)$$

Therefore;

$$C_T = \frac{[H^+][HCO_3^-]}{K_1} f_1 + HCO_3^- = \frac{H+f_1}{K_1} + 1 \quad HCO_3^- \quad (F.2.53)$$

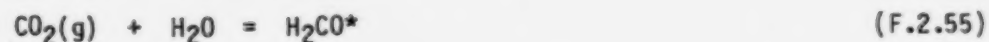
or,

$$HCO_3^- = \frac{K_1 C_T}{10^{-pH} f_1 + K_1} \quad (F.2.54)$$

Substitution of HCO_3^- term into equation (F.2.52) gives HCO_3^- as a function of C_T where C_T is found by mass balance.

Open System

In this case, the partial pressure of carbon dioxide (PCO_2) is constant. The formation of carbonic acid from gaseous CO_2 is represented by:



The equilibrium relationship between gaseous CO_2 and carbonic acid is called Henry's Law, defined as:

$$H_2CO_3^* = P_{CO2} \cdot K_H \quad (F.2.56)$$

Substitution into equation F.2.52 and rearrangement gives;

$$(HCO_3^-) = K_1 K_H f_1 10^{pH} \cdot P_{CO2} \quad (F.2.57)$$

F.2.3 Mathematical Solution for pH

Mathematical solution of the electroneutrality equation for pH (Equation F.2.22) requires use of an iterative technique. The Newton-Raphson Method was initially employed to obtain the root of equation (F.2.22). This method requires the determination of the derivative of the mass balance expression. This method has been used successfully by SENES (1986) for their probabilistic assessment of pyritic tailings. It was generally an excellent technique, for this work, but did not converge in certain cases. The lack of convergence is due to the inability to obtain exact differentials for certain complexes because the development of the derivations did not fully take into account the simultaneous interdependencies of all variables. This would have required use of matrix algebra and used of equilibrium codes such as MINTEQA. The use of such techniques was beyond the scope of this project.

A second method, the secant method was also tried. The secant method evaluates the slope of the function and does not require the algebraic formulation of the derivative of the function. Unfortunately this method also proved to be ineffective in the determination of the pH because of its asymptotic approach to the root of the function. Figure F.5 presents the convergence of the function.

Accordingly, a search routine was used to find the root of Equation (F.2.22). Two alternatives were considered: one in which successive increasing pH values are considered until the function changes sign and then the smaller increments are used; the second in which a standard small increment (delete pH=0.5) is searched and the root taken as the pH value at which the sign of the function changes. For this work, second routine was chosen for ease of coding. Future

work would substantially decrease the computer time involved by selected the first technique.

F.3 Parameter Distributions

The following section describes the parameters which are used to calculate the pH, aqueous concentrations and solid phase concentrations. Table F.3.1 lists the probability distribution types and descriptions and the computer source symbol assigned to the parameters.

F.3.1 Solubility Constants

Solubility constants have a lognormal probability distribution with a range equal to 3 times the standard deviation of the pK_{SO} ($-\log$ of the solubility constant). Two different values for standard deviation are used. For calcite and gypsum, solubility constants are reasonably well established. Evaluation of the literature suggested that the pK values are known with a standard deviation of 10% (BEAK, 1986). These values were also used herein. For other solids (e.g. basaluminite, ferric hydroxide), the mineral structure is less known. The solids can convert from an amorphous to a crystalline form over a time-scale of months to years with an associated change in solubility produced of 2-3 orders of magnitude (e.g., see Eq. F.2.1a; F.2.1b). For such solids, a standard deviation of 50% for the pK_{SO} was assigned.

F.3.2 Complexation Constants

Complexation constants are also not precisely known, having measured relative standard deviation of 10-20% for the pK ($-\log$ of the complexation constant). For purposes of this project they were assumed not to be probabilistic variables.

Table F.3.1

AQUEOUS SPECIATION MODULE PARAMETERS

Symbol	Description	Units	Nominal	Probabilistic	Origin	Computer Code
f_{ALOH}	empirical coefficient for aluminum in acid convergence front	(unitless)	0.075	T(0.01,0.075,0.6)		FALOH
K_H	Henry's law constant	($\text{m}^3 \cdot \text{m}^{-3}$)	23.6	C(23.6)	Input	HENRY
CHS04	T.S. constant for HSO_4		1.26E-2	C(1.26x10 ⁻²)	Input	CHS04
CCAS04	T.S. constant for CASO_4		316.23	C(316.23)	Input	CCAS04
CALS04	T.S. constant for ALSO_4	($\text{mol} \cdot \text{L}^{-1}$) ⁻¹	1047.13	C(1047.13)	Input	CALS04
CFE0H	T.S. constant for FEOH		6.46x10 ⁻³	C(6.46x10 ⁻³)	Input	CFE0H
CFE0H2	T.S. constant for FEOH_2		2.14x10 ⁻⁶	C(2.14x10 ⁻⁶)	Input	CFE0H2
CFES04	T.S. constant for FESO_4		8317.64	C(8317.64)	Input	CFES04
CFE0H3	T.S. constant for FEOH_3		1x10 ⁻¹²	C(1x10 ⁻¹²)	Input	CFE0H3
CAL0H3	T.S. constant for ALOH_3	($\text{mol} \cdot \text{L}^{-1}$) ²	1x10 ⁻¹⁵	C(1x10 ⁻¹⁵)	Input	CAL0H3
f_1	activity coefficient		0.84	T(0.67,0.84,1.01)	Input	F1
f_2	activity coefficient		0.499	T(0.399,0.499,0.599)	Input	F2
f_3	activity coefficient		0.201	T(0.18,0.201,0.22)	Input	F3
K_{CAS04}	gypsum	($\text{mol} \cdot \text{L}^{-1}$) ²	2.4x10 ⁻⁵	LN(2.4x10 ⁻⁵ , 1.05, 2.14x10 ⁻⁵ , 2.75x10 ⁻⁵)	Input	KCAS04
K_1	dissociation constant for HCO_3°	($\text{mol} \cdot \text{L}^{-1}$)	5.012x10 ⁻⁷	C(5.01x10 ⁻⁷)	Input	K1
K_2	dissociation constant for HCO_3^-	($\text{mol} \cdot \text{L}^{-1}$)	5.012x10 ⁻¹¹	C(5.012x10 ⁻¹¹)	Input	K2
K_{CACO_3}	calcite solubility	($\text{mol} \cdot \text{L}^{-1}$) ²	4.48x10 ⁻⁹	LN(4.48x10 ⁻⁹ , 1.05, 3.88x10 ⁻⁹ , 5.13x10 ⁻⁹)	Input	KCAC03
K_{FEOOH}	FEOOH solubility		3.98x10 ¹	LN(3.98x10 ¹ , 3.16, 1.27, 1.27x10 ³)	Input	KFEOOH
CAL0H ₂	T.S. constant for ALOH_2	($\text{mol} \cdot \text{L}^{-1}$)	5.0x10 ⁻¹⁰	C(5.0x10 ⁻¹⁰)	Input	CAL0H2
CAL0H	T.S. constant for ALOH	($\text{mol} \cdot \text{L}^{-1}$)	1.07x10 ⁻⁵	C(1.07x10 ⁻⁵)	Input	CAL0H
KBAS	Log Basaluminite solubility constant		22.7	LN(22.7, 1.02, 21.7, 23.7)	Input	KBAS
P_{CO_2}	carbon dioxide partial pressure	($\text{mol} \cdot \text{L}^{-1}$)	calculated	calculated	Initial	CO2(i,t)
Ca^{2+}	Calcium concentration	($\text{mol} \cdot \text{L}^{-1}$)	calculated	calculated	Transport	CA(i,t)
H^+	Hydronium ion concentration	($\text{mol} \cdot \text{L}^{-1}$)	calculated	calculated	Speciation	HI(i,t)
S_T	total dissolved sulphate	($\text{mol} \cdot \text{L}^{-1}$)	calculated	calculated	Transport	SO4T(i,t)

Table F.1, cont'd.

<u>Symbol</u>	<u>Description</u>	<u>Units</u>	<u>Nominal</u>	<u>Probabilistic</u>	<u>Origin</u>	<u>Computer Code</u>
C _T	total inorganic carbon	(mol.L ⁻¹)	calculated	calculated	Transport	CT(1,t)
SO ₄	sulphate concentration	(mol.L ⁻¹)	calculated	calculated	Transport	SO4(1,t)
HCO ₃	carbonate concentration	(mol.L ⁻¹)	calculated	calculated	Transport	HCO3(1,t)
Fe ²⁺	ferrous ion concentration	(mol.L ⁻¹)	calculated	calculated	Transport	FE2(1,t)
Fe ³⁺	ferric ion concentration	(mol.L ⁻¹)	calculated	calculated	Transport	FE3(1,t)
Al ³⁺	aqueous aluminum concentration	(mol.L ⁻¹)	calculated	calculated	Transport	AL3(1,t)
Al _T	total aqueous aluminum concentration	(mol.L ⁻¹)	calculated	calculated	Transport	ALT(1,t)
ALUM	aluminum species present in C.B. eq.	(mol.L ⁻¹)	calculated	calculated	Speciation	ALUM
IRON3	ferric iron species present in C.B. eq.	(mol.L ⁻¹)	calculated	calculated	Speciation	IRON
SULF	sulfate species present in C.B. eq.	(mol.L ⁻¹)	calculated	calculated	Speciation	SULF
AL(OH) ₃	aluminum solid	(mol.m ⁻³)	calculated	calculated	Transport	ALOH3(1,t)
Fe(OH) ₃	iron solid	(mol.m ⁻³)	calculated	calculated	Transport	FEOH3(1,t)
XKFe3	fraction of Fe ³⁺ from redox reactions	(unitless)	0.01	T(0.005,0.01,0.05)	Input	XKFE3

Notes

T.S. = thermodynamic stability constants.
 C.B. = charge balance equation
 i = indicates the months of the year
 t = indicates the overall time period

Key to ProbabilisticParameter values:

- C - Constant (single value)
- LN - Lognormal (geo. mean, geo. Std. dev., min., max.)
- N - Normal (mean, Std. dev., min., max.)
- T - Triangular (min., mode, max.)
- U - Uniform (min., max.)

F.3.3 Activity Coefficients

Activity coefficients were assigned probabilistic attributes based upon the typically computed ionic strength of the porewater, the Debye-Huckel equation, (see BEAK, 1986), and an assumed +10% standard deviation for their values.

F.4 Algorithm Calibration/Validation

Simplification of the complex chemical equilibria was used because such simplification are appropriate and because they minimize computational effort. However, simplification implies that some degree of error will be involved. The chemical component of the code was therefore tested by comparing predicted values against those determined by complete and more comprehensive models.

The comparative models used here were MINTEQ (Felmy et al., 1984), which is a member of the MINEQL family of computer speciation programs that are capable of computing equilibrium with solids, and the Reaction Path Simulation model, of AECL. Results from the Reaction Path Simulation Model are presented in Appendix G.

MINTEQ

MINTEQ calculates solution and solid phase equilibria for all solid phases, and soluble species present. MINTEQ, however, requires more computational time and storage space to perform the necessary computations. MINTEQ is presently a canned program that has been subjected to rigorous quality control checks and extensive code verification. It is therefore a good model against which to verify the present model code. In essence, it should give exactly the same answers as the present model, provided that simplifications of the present model are appropriate. MINTEQ cannot be used to compare calculations where kinetic's control solid-solution relationships because it is based exclusively upon equilibrium relationships.

The most critical aspect of the model is the calculation of pH. The pH is



affected by the acid generation rate and reactions with various solids that buffer the pH as they dissolve. Numerous comparisons were conducted between the calculations of the present model and those from MINTEQ, including conditions with different combinations of solid phases present. A summary of the important comparisons is given in Table F.4.1. The MINTEQ calculations show that when calcite is present, the pH remains about 6.5. After calcite has been depleted, the basaluminite solid phase controls pH to levels of about 4. Finally, when goethite is the only remaining solid buffer, the pH decreases to levels around 2.

The calculations of our kinetics model compare quite well with those of MINTEQ. For the first two conditions only small discrepancies exist when comparing the model Fe^{3+} and Al_T concentrations. For the conditions of calcite/aluminum hydroxide absence the model predicts a lower pH range and a higher Fe^{3+} total concentration than the MINTEQ model. But the calculations of our model for Fe^{3+} and pH compare favourably however with field data from the Nordic tailings. Hence, the values predicted by MINTEQ may indicate that the Nordic field data is not at equilibrium with the appropriate solid phases.

F.5 Sensitivity/Uncertainty Analysis

The results of a sensitivity/uncertainty analyses are presented in Tables F.5.1 to F.5.12 for layers 1, 5 and 11 (0.2m, 1.0m, and 2.2m) and time period 13, 18, 121 and 126 months. The tables contain the influence of inputs on parameters calculated in the solute transport and aqueous speciation module. These parameters include monthly acid flux (aflux), total acid flux (atotal), pH and aqueous concentrations.

Table F.4.1

COMPARISON OF MINTEQ CALCULATIONS TO MODEL PREDICTIONS

Scenario [*]	Components	Predicted Values ^{**}		
		Model ^{***}		
		MINTEQ	Winter (February)	Summer (June)
Calcite	pH	6.48	6.29-6.69	6.32-6.83
	Fe ^{III}	9.9×10^{-12}	6.1×10^{-11} - 9.2×10^{-11}	5.6×10^{-11} - 8.8×10^{-11}
	Al ^T	1.5×10^{-5}	2.7×10^{-6} - 3.2×10^{-6}	2.7×10^{-6} - 3.2×10^{-6}
Basaluminite (calcite depleted)	pH	3.95	3.65-4.25	3.5-3.8
	Fe ^{III}	4.65×10^{-9}	1.1×10^{-8} - 2.3×10^{-7}	5.0×10^{-8} - 7.2×10^{-7}
	Al ^T	2.59×10^{-3}	3.1×10^{-3} - 4.5×10^{-2}	9.3×10^{-3} - 1.0×10^{-1}
Goethite (calcite and Basaluminite depleted)	pH	2.35-1.95	1.8-1.9	1.65-1.8
	Fe ^{III}	4.45×10^{-5}	1.7×10^{-2} - 4.5×10^{-2}	3.8×10^{-2} - 9.1×10^{-2}

Notes

* gypsum is present in all cases.

** predicted values are in moles/L except pH.

*** deterministic simulation employing nominal values.

Table F.5.1
Sensitivity Analysis
on the Monthly Acid Flux

SENSITIVITY OF INPUTS ON AFLUX

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.916E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.659E-02	0.786E-01
2	0.790E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.166E-01	0.791E-01
3	0.719E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.503E-01	0.179E+00
4	0.675E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.410E-01	0.126E+00
5	0.647E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.275E-01	0.781E-01
6	0.636E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.265E-01	0.727E-01
LAYER 5 FOR MONTH 13								
1	0.947E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.962E-01	0.180E+01
2	0.783E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.110E+00	0.505E+00
3	0.748E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.285E+00	0.113E+01
4	0.613E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.241E+00	0.623E+00
5	0.423E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.263E+00	0.456E+00
6	0.291E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.273E+00	0.385E+00
7	0.278E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.210E+00	0.291E+00
8	0.233E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.276E+00	0.360E+00
LAYER 11 FOR MONTH 13								
1	0.951E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.127E+00	0.257E+01
2	0.900E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.104E+00	0.104E+01
3	0.847E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.521E+00	0.340E+01
4	0.648E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.249E+00	0.707E+00
5	0.481E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.472E+00	0.909E+00
6	0.450E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.475E+00	0.864E+00
7	0.447E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.479E+00	0.866E+00
8	0.353E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.505E+00	0.780E+00
9	0.341E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.493E+00	0.748E+00
10	0.305E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.426E+00	0.613E+00
11	0.236E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.504E+00	0.660E+00
12	0.215E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.496E+00	0.631E+00
13	0.203E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.507E+00	0.636E+00
14	0.201E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.507E+00	0.635E+00
15	0.137E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.512E+00	0.594E+00
LAYER 1 FOR MONTH 18								
1	0.917E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.383E+00	0.461E+01
2	0.903E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.134E+01	0.138E+02
3	0.864E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.683E+00	0.502E+01
4	0.755E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.785E+00	0.320E+01
5	0.433E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.324E+01	0.571E+01
6	0.289E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.334E+01	0.469E+01
7	0.224E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.407E+01	0.525E+01
8	0.165E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.411E+01	0.492E+01
9	0.137E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.431E+01	0.500E+01
10	0.123E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.424E+01	0.484E+01
LAYER 5 FOR MONTH 18								
1	0.942E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.409E+00	0.706E+01

SENSITIVITY OF INPUTS ON AFLUX

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
2	0.784E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.447E+00	0.207E+01
3	0.597E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.101E+01	0.250E+01
4	0.592E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.118E+01	0.288E+01
5	0.567E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.500E+00	0.115E+01
6	0.465E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.107E+01	0.200E+01
7	0.363E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.637E+00	0.100E+01
8	0.328E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.813E+00	0.121E+01
9	0.244E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.113E+01	0.150E+01
10	0.147E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.988E+00	0.116E+01
11	0.132E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.115E+01	0.133E+01

LAYER 11 FOR MONTH 18

1	0.975E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.856E+00	0.341E+02
2	0.900E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.605E+00	0.605E+01
3	0.885E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.302E+01	0.263E+02
4	0.515E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.156E+01	0.321E+01
5	0.464E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.275E+01	0.513E+01
6	0.458E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.288E+01	0.531E+01
7	0.413E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.280E+01	0.477E+01
8	0.411E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.280E+01	0.476E+01
9	0.396E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.282E+01	0.466E+01
10	0.305E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.247E+01	0.356E+01
11	0.261E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.291E+01	0.394E+01
12	0.240E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.285E+01	0.374E+01
13	0.177E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.295E+01	0.359E+01
14	0.143E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.297E+01	0.346E+01

LAYER 1 FOR MONTH 121

1	0.979E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.160E-03	0.745E-02
2	0.599E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.356E-02	0.887E-02
3	0.426E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.533E-02	0.929E-02
4	0.404E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.402E-02	0.674E-02
5	0.393E+00	-	FALDN	0.100E-01	0.750E-01	0.600E+00	0.543E-02	0.894E-02
6	0.343E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.423E-02	0.644E-02
7	0.233E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.482E-02	0.629E-02
8	0.210E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.520E-02	0.658E-02
9	0.197E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.160E-03	0.199E-03
10	0.173E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.472E-02	0.571E-02

LAYER 5 FOR MONTH 121

1	0.878E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.769E-01	0.629E+00
2	0.760E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.171E+00	0.714E+00
3	0.677E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.256E+00	0.793E+00
4	0.593E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.145E+00	0.357E+00
5	0.578E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.153E+00	0.362E+00
6	0.486E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.320E+00	0.623E+00
7	0.476E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.260E+00	0.497E+00
8	0.461E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.322E+00	0.598E+00
9	0.326E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.253E+00	0.376E+00
10	0.325E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.313E+00	0.463E+00



SENSITIVITY OF INPUTS ON AFLUX

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
11	0.292E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.314E+00	0.443E+00
12	0.268E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.270E+00	0.369E+00
13	0.265E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.318E+00	0.433E+00

LAYER 11 FOR MONTH 121

1	0.844E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.532E-01	0.341E+00
2	0.806E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.308E+00	0.159E+01
3	0.651E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.658E+00	0.188E+01
4	0.629E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.743E+00	0.200E+01
5	0.594E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.761E+00	0.187E+01
6	0.551E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.825E+00	0.184E+01
7	0.518E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.782E+00	0.162E+01
8	0.515E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.758E+00	0.156E+01
9	0.514E+00	-	FALON	0.100E-01	0.750E-01	0.600E+00	0.826E+00	0.170E+01
10	0.512E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.166E+01	0.340E+01
11	0.508E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.778E+00	0.158E+01
12	0.496E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.778E+00	0.154E+01
13	0.488E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.789E+00	0.154E+01
14	0.470E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.817E+00	0.154E+01
15	0.456E+00	+	IALOH3	0.140E-02	0.230E-02	0.320E-02	0.835E+00	0.154E+01
16	0.388E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.838E+00	0.137E+01
17	0.334E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.623E+00	0.935E+00
18	0.330E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.645E+00	0.963E+00
19	0.236E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.771E+00	0.101E+01
20	0.234E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.660E+00	0.862E+00
21	0.214E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.757E+00	0.963E+00
22	0.179E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.770E+00	0.938E+00
23	0.177E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.768E+00	0.934E+00
24	0.123E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.740E+00	0.843E+00

LAYER 1 FOR MONTH 126

1	0.999E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.617E-03	0.593E+00
1	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.617E-03	0.814E+00
2	0.442E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.660E+00	0.118E+01
3	0.438E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.567E+00	0.101E+01
4	0.334E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.526E+00	0.790E+00
5	0.263E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.587E+00	0.796E+00
6	0.188E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.637E+00	0.784E+00
7	0.180E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.544E+00	0.664E+00
8	0.144E+00	-	FALON	0.100E-01	0.750E-01	0.600E+00	0.650E+00	0.759E+00
9	0.134E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.672E+00	0.777E+00

LAYER 5 FOR MONTH 126

1	0.982E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.179E-01	0.102E+01
2	0.797E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.433E+00	0.213E+01
3	0.657E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.458E+00	0.134E+01
4	0.544E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.598E+00	0.131E+01
5	0.509E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.489E+00	0.996E+00
6	0.450E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.905E+00	0.165E+01
7	0.421E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.778E+00	0.134E+01

SENSITIVITY OF INPUTS ON AFLUX

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
8	0.355E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.673E+00	0.104E+01
9	0.314E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.706E+00	0.103E+01
10	0.291E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.817E+00	0.115E+01
11	0.232E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.896E+00	0.117E+01
12	0.144E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.907E+00	0.106E+01
13	0.118E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.848E+00	0.961E+00
13	0.118E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.200E+01	0.227E+01

LAYER 11 FOR MONTH 126

1	0.900E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.975E+00	0.977E+01
2	0.723E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.128E+01	0.462E+01
3	0.621E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.217E+01	0.573E+01
4	0.604E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.486E+01	0.123E+02
5	0.594E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.361E+01	0.890E+01
6	0.473E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.921E+01	0.175E+02
7	0.465E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.490E+01	0.916E+01
8	0.442E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.448E+01	0.803E+01
9	0.424E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.454E+01	0.788E+01
10	0.421E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.459E+01	0.793E+01
11	0.373E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.460E+01	0.734E+01
12	0.367E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.376E+01	0.594E+01
13	0.321E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.400E+01	0.589E+01
14	0.297E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.484E+01	0.688E+01
15	0.185E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.479E+01	0.588E+01
16	0.154E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.480E+01	0.568E+01
17	0.128E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.484E+01	0.555E+01
18	0.118E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.463E+01	0.525E+01
19	0.110E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.485E+01	0.545E+01
20	0.106E+00	-	FALON	0.100E-01	0.750E-01	0.600E+00	0.494E+01	0.553E+01



Table F.5.2
Sensitivity Analysis
Al³⁺ Concentration

SENSITIVITY OF INPUTS ON AL3

	RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13									
	1	0.100E+01	+	XP	0.320E-03	0.160E-02	0.780E-02	0.161E-08	0.368E-03
	1	0.100E+01	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.167E-08	0.649E-03
	1	0.100E+01	-	SATCT	0.100E-02	0.350E-02	0.100E-01	0.162E-08	0.648E-03
	1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.194E-08	0.176E-04
	2	0.996E+00	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.161E-08	0.371E-06
	3	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.905E-09	0.286E-08
	4	0.584E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.743E-09	0.179E-08
	5	0.294E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.136E-08	0.192E-08
	6	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.147E-08	0.180E-08
	7	0.140E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.148E-08	0.172E-08
LAYER 5 FOR MONTH 13									
	1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.478E-09	0.736E-02
	1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.138E-08	0.995E-02
	2	0.741E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.153E-09	0.592E-09
	3	0.719E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.131E-09	0.465E-09
	4	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.269E-09	0.850E-09
	5	0.666E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.187E-09	0.559E-09
	6	0.535E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.246E-09	0.530E-09
	7	0.375E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.316E-09	0.507E-09
	8	0.349E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.390E-09	0.599E-09
	9	0.302E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.348E-09	0.499E-09
	10	0.290E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.404E-09	0.569E-09
	11	0.228E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.415E-09	0.538E-09
	12	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.437E-09	0.534E-09
LAYER 11 FOR MONTH 13									
	1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.836E-10	0.749E-02
	2	0.996E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.566E-12	0.136E-09
	3	0.994E+00	+	SATCT	0.100E-02	0.350E-02	0.100E-01	0.170E-11	0.298E-09
	4	0.842E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.168E-10	0.106E-09
	5	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.470E-10	0.149E-09
	6	0.548E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.538E-10	0.119E-09
	7	0.413E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.643E-10	0.109E-09
	8	0.241E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.667E-10	0.878E-10
	9	0.230E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.725E-10	0.942E-10
	10	0.227E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.734E-10	0.950E-10
	11	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.764E-10	0.934E-10
	12	0.168E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.925E-10	0.111E-09
	13	0.152E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.771E-10	0.909E-10
	14	0.138E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.733E-10	0.850E-10
	15	0.114E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.751E-10	0.848E-10
LAYER 1 FOR MONTH 18									
	1	0.100E+01	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.109E-08	0.799E-02
	1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.978E-09	0.651E-02
	2	0.999E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.151E-08	0.223E-05
	3	0.636E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.422E-02	0.116E-01

SENSITIVITY OF INPUTS ON AL3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
4	0.618E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.522E-02	0.137E-01
5	0.393E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.649E-02	0.107E-01
6	0.234E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.847E-02	0.110E-01
7	0.207E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.644E-02	0.813E-02
8	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.750E-02	0.917E-02

LAYER 5 FOR MONTH 18

1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.692E-09	0.668E-02
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.153E-08	0.728E-02
2	0.795E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.138E-09	0.671E-09
3	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.391E-09	0.123E-08
4	0.680E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.260E-09	0.812E-09
5	0.613E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.305E-09	0.790E-09
6	0.534E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.357E-09	0.765E-09
7	0.488E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.707E-09	0.138E-08
8	0.311E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.818E-09	0.119E-08
9	0.294E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.585E-09	0.829E-09
10	0.280E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.592E-09	0.823E-09
11	0.276E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.522E-09	0.721E-09
12	0.205E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.613E-09	0.771E-09
13	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.634E-09	0.775E-09
14	0.149E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.704E-09	0.828E-09
15	0.147E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.603E-09	0.707E-09

LAYER 11 FOR MONTH 18

1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.134E-09	0.966E-02
2	0.998E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.281E-12	0.152E-09
3	0.994E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.289E-11	0.482E-09
4	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.754E-10	0.238E-09
5	0.546E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.865E-10	0.190E-09
6	0.411E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.103E-09	0.175E-09
7	0.184E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.120E-09	0.147E-09
8	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.122E-09	0.150E-09
9	0.126E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.119E-09	0.136E-09
10	0.109E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.121E-09	0.136E-09
11	0.108E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.116E-09	0.130E-09

LAYER 1 FOR MONTH 121

1	0.999E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.134E-07	0.117E-04
2	0.913E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.922E-05	0.106E-03
3	0.728E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.134E-07	0.493E-07
4	0.476E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.122E-04	0.233E-04
5	0.295E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.159E-04	0.226E-04
6	0.219E+00	+	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.181E-04	0.232E-04
7	0.182E+00	-	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.176E-04	0.215E-04
8	0.153E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.181E-04	0.214E-04
9	0.125E+00	-	IALON3	0.140E-02	0.230E-02	0.320E-02	0.182E-04	0.207E-04
10	0.121E+00	-	FALON	0.100E-01	0.750E-01	0.600E+00	0.204E-04	0.233E-04
11	0.118E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.183E-04	0.208E-04
	0.118E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.183E-04	0.208E-04

SENSITIVITY OF INPUTS ON AL3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
12	0.105E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.183E-04	0.205E-04
13	0.105E+00	-	WT1	0.450E+00	0.500E+00	0.550E+00	0.183E-04	0.205E-04
14	0.101E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.195E-04	0.217E-04

LAYER 5 FOR MONTH 121

1	0.993E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.410E-04	0.626E-02
2	0.992E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.313E-04	0.392E-02
3	0.974E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.286E-04	0.110E-02
4	0.706E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.300E-04	0.102E-03
5	0.603E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.328E-04	0.826E-04
6	0.361E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.292E-04	0.456E-04
7	0.221E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.343E-04	0.440E-04
8	0.167E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.373E-04	0.448E-04
9	0.148E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.374E-04	0.439E-04
9	0.148E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.359E-04	0.421E-04
10	0.139E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.386E-04	0.448E-04
11	0.134E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.369E-04	0.425E-04
12	0.119E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.385E-04	0.437E-04
13	0.101E+00	-	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.374E-04	0.417E-04

LAYER 11 FOR MONTH 121

1	0.100E+01	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.159E-11	0.437E-04
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.560E-12	0.231E-04
1	0.100E+01	+	FALDH	0.100E-01	0.750E-01	0.600E+00	0.212E-11	0.436E-04
1	0.100E+01	-	ME1	-0.500E-01	-0.500E+00	-0.150E+01	0.643E-10	0.840E-03
2	0.400E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.580E-02	0.966E-02
3	0.374E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.502E-02	0.802E-02
4	0.255E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.507E-02	0.682E-02
5	0.244E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.467E-02	0.617E-02
6	0.235E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.593E-02	0.775E-02
7	0.234E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.593E-02	0.774E-02
8	0.226E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.595E-02	0.769E-02
9	0.219E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.592E-02	0.759E-02
10	0.217E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.450E-02	0.575E-02
11	0.193E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.620E-02	0.769E-02
12	0.181E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.540E-02	0.659E-02
13	0.176E+00	+	WT1	0.450E+00	0.500E+00	0.550E+00	0.486E-02	0.590E-02
14	0.172E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.489E-02	0.591E-02
15	0.166E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.493E-02	0.591E-02
16	0.163E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.493E-02	0.589E-02
17	0.162E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.493E-02	0.588E-02
18	0.155E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.493E-02	0.584E-02
19	0.150E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.493E-02	0.580E-02
20	0.100E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.563E-02	0.626E-02

LAYER 1 FOR MONTH 126

1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.223E-08	0.259E-02
2	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.223E-08	0.323E-05
3	0.874E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.167E-05	0.133E-04
4	0.209E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.297E-05	0.375E-05

SENSITIVITY OF INPUTS ON AL3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
5	0.182E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.278E-05	0.340E-05
6	0.113E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.319E-05	0.360E-05

LAYER 5 FOR MONTH 126

1	0.996E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.221E-04	0.531E-02
2	0.990E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.416E-04	0.405E-02
3	0.888E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.421E-05	0.375E-04
4	0.723E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.316E-04	0.115E-03
5	0.714E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.321E-04	0.113E-03
6	0.685E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.209E-04	0.662E-04
7	0.216E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.342E-04	0.436E-04
8	0.166E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.370E-04	0.444E-04

LAYER 11 FOR MONTH 126

1	0.100E+01	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.843E-10	0.606E-04
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.178E-10	0.314E-02
2	0.994E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.437E-04	0.783E-02
3	0.992E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.615E-04	0.781E-02
4	0.332E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.631E-02	0.945E-02
5	0.329E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.905E-02	0.120E-01
6	0.324E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.521E-02	0.770E-02
7	0.248E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.821E-02	0.109E-01
8	0.238E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.808E-02	0.106E-01
9	0.206E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.806E-02	0.102E-01
10	0.181E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.733E-02	0.895E-02
11	0.180E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.817E-02	0.997E-02
12	0.162E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.817E-02	0.976E-02
13	0.161E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.820E-02	0.977E-02
14	0.154E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.823E-02	0.972E-02
15	0.142E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.804E-02	0.937E-02
16	0.114E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.763E-02	0.861E-02

Table F.5.3
Sensitivity Analysis
on Total Al Concentration

SENSITIVITY OF INPUTS ON ALT

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.998E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.318E-05	0.158E-02
1	0.998E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.317E-05	0.158E-02
2	0.996E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.316E-05	0.888E-03
3	0.936E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.322E-05	0.499E-04
4	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.178E-05	0.563E-05
5	0.258E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.317E-05	0.427E-05
LAYER 5 FOR MONTH 13								
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.293E-05	0.686E-01
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.315E-05	0.116E+00
2	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.165E-05	0.521E-05
3	0.366E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.293E-05	0.462E-05
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.469E-05	0.190E+00
2	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.263E-05	0.833E-05
3	0.582E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.390E-05	0.931E-05
4	0.281E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.461E-05	0.641E-05
5	0.156E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.434E-05	0.515E-05
LAYER 1 FOR MONTH 18								
1	0.100E+01	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.315E-05	0.559E-01
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.313E-05	0.345E-01
2	0.929E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.225E-01	0.315E+00
3	0.913E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.146E-01	0.167E+00
4	0.627E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.323E-05	0.867E-05
5	0.530E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.347E-01	0.738E-01
6	0.341E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.353E-01	0.535E-01
7	0.147E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.491E-01	0.575E-01
8	0.115E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.490E-01	0.554E-01
9	0.106E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.493E-01	0.552E-01
LAYER 5 FOR MONTH 18								
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.304E-05	0.326E-01
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.321E-05	0.704E-01
2	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.171E-05	0.540E-05
3	0.343E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.303E-05	0.461E-05
LAYER 11 FOR MONTH 18								
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.461E-05	0.280E+00
2	0.684E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.259E-05	0.821E-05
3	0.567E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.388E-05	0.395E-05
4	0.323E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.460E-05	0.679E-05
5	0.156E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.428E-05	0.507E-05
LAYER 1 FOR MONTH 121								
1	0.918E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.204E-04	0.248E-03
2	0.877E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.427E-05	0.346E-04

SENSITIVITY OF INPUTS ON ALT

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
3	0.357E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.299E-04	0.464E-04
4	0.114E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.411E-04	0.464E-04
5	0.102E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.404E-04	0.450E-04

LAYER 5 FOR MONTH 121

1	0.997E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.119E-03	0.378E-01
2	0.993E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.117E-03	0.168E-01
3	0.959E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.120E-03	0.295E-02
4	0.718E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.926E-04	0.328E-03
5	0.713E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.930E-04	0.324E-03
6	0.204E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.115E-03	0.144E-03
7	0.178E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.116E-03	0.141E-03
8	0.175E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.116E-03	0.140E-03

LAYER 11 FOR MONTH 121

1	0.998E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.473E-05	0.218E-02
2	0.971E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.592E-05	0.203E-03
3	0.971E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.579E-05	0.203E-03
4	0.960E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.642E-05	0.162E-03
5	0.595E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.420E-01	0.104E+00
6	0.568E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.427E-01	0.988E-01
7	0.522E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.454E-01	0.950E-01
8	0.515E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.390E-01	0.804E-01
9	0.418E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.474E-01	0.814E-01
10	0.396E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.434E-01	0.719E-01
11	0.387E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.433E-01	0.706E-01
12	0.376E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.433E-01	0.694E-01
13	0.372E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.385E-01	0.614E-01
14	0.370E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.437E-01	0.693E-01
15	0.368E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.438E-01	0.693E-01
16	0.355E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.446E-01	0.692E-01
17	0.345E+00	+	IALON3	0.140E-02	0.230E-02	0.320E-02	0.453E-01	0.691E-01
18	0.325E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.312E-01	0.462E-01
19	0.321E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.430E-01	0.633E-01
20	0.307E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.425E-01	0.614E-01
21	0.287E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.430E-01	0.603E-01
22	0.286E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.429E-01	0.601E-01
23	0.235E+00	+	KFEEDOM	0.127E+01	0.398E+02	0.127E+04	0.641E-01	0.838E-01
24	0.227E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.377E-01	0.488E-01
25	0.177E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.395E-01	0.479E-01

LAYER 1 FOR MONTH 126

1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.339E-05	0.710E-02
2	0.905E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.407E-05	0.431E-04
3	0.595E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.339E-05	0.838E-05

LAYER 5 FOR MONTH 126

1	0.997E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.695E-04	0.217E-01
2	0.993E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.107E-03	0.157E-01
3	0.913E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.942E-05	0.108E-03

SENSITIVITY OF INPUTS ON ALT

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
4	0.739E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.815E-04	0.312E-03
5	0.726E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.827E-04	0.302E-03
6	0.602E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.637E-04	0.160E-03
7	0.276E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.103E-03	0.142E-03
8	0.134E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.106E-03	0.122E-03
9	0.106E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.106E-03	0.119E-03

LAYER 11 FOR MONTH 126

1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.503E-05	0.111E-01
2	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.244E-03	0.168E+00
3	0.996E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.247E-03	0.590E-01
4	0.981E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.468E-05	0.247E-03
5	0.641E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.548E-01	0.153E+00
6	0.632E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.370E-01	0.101E+00
7	0.630E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.226E-01	0.610E-01
8	0.467E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.550E-01	0.103E+00
9	0.444E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.521E-01	0.936E-01
10	0.431E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.525E-01	0.923E-01
11	0.430E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.529E-01	0.927E-01
12	0.397E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.529E-01	0.878E-01
13	0.348E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.546E-01	0.838E-01
14	0.279E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.543E-01	0.754E-01
15	0.251E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.468E-01	0.625E-01
16	0.218E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.486E-01	0.622E-01
17	0.140E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.507E-01	0.590E-01
18	0.104E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.544E-01	0.607E-01

Table F.5.4
Sensitivity Analysis
on Cumulative Acid Flux

SENSITIVITY OF INPUTS ON ATOTAL

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.907E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.454E+01	0.486E+02
2	0.681E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.760E+01	0.238E+02
3	0.638E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.737E+01	0.204E+02
4	0.380E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.684E+01	0.110E+02
5	0.180E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.693E+01	0.844E+01
6	0.141E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.708E+01	0.824E+01
7	0.104E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.723E+01	0.806E+01
8	0.103E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.723E+01	0.806E+01
LAYER 5 FOR MONTH 13								
1	0.960E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.799E+01	0.202E+03
2	0.753E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.290E+02	0.118E+03
3	0.439E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.273E+02	0.487E+02
4	0.383E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.273E+02	0.443E+02
5	0.308E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.279E+02	0.403E+02
6	0.303E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.278E+02	0.399E+02
7	0.279E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.242E+02	0.336E+02
8	0.247E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.289E+02	0.384E+02
9	0.238E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.260E+02	0.342E+02
10	0.237E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.291E+02	0.381E+02
11	0.215E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.233E+02	0.297E+02
12	0.208E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.265E+02	0.335E+02
13	0.180E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.265E+02	0.323E+02
14	0.133E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.283E+02	0.327E+02
15	0.126E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.283E+02	0.323E+02
16	0.100E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.293E+02	0.326E+02
LAYER 11 FOR MONTH 13								
1	0.856E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.316E+02	0.219E+03
2	0.813E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.773E+01	0.413E+02
3	0.745E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.935E+01	0.366E+02
4	0.622E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.270E+02	0.716E+02
5	0.536E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.281E+02	0.605E+02
6	0.508E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.285E+02	0.579E+02
7	0.295E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.260E+02	0.369E+02
8	0.280E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.276E+02	0.384E+02
9	0.207E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.301E+02	0.380E+02
9	0.207E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.293E+02	0.370E+02
10	0.204E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.318E+02	0.399E+02
11	0.189E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.290E+02	0.357E+02
12	0.180E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.289E+02	0.352E+02
13	0.137E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.305E+02	0.353E+02
LAYER 1 FOR MONTH 18								
1	0.886E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.661E+01	0.581E+02
2	0.776E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.108E+02	0.482E+02
3	0.645E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.105E+02	0.295E+02
4	0.538E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.953E+01	0.206E+02



SENSITIVITY OF INPUTS ON ATOTAL

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
5	0.324E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.128E+02	0.190E+02
6	0.226E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.129E+02	0.167E+02
7	0.170E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.148E+02	0.178E+02
8	0.121E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.143E+02	0.163E+02
9	0.120E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.143E+02	0.162E+02
10	0.113E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.154E+02	0.173E+02
11	0.106E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.145E+02	0.162E+02

LAYER 5 FOR MONTH 18

1	0.955E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.105E+02	0.232E+03
2	0.700E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.374E+02	0.125E+03
3	0.432E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.348E+02	0.613E+02
4	0.375E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.357E+02	0.571E+02
5	0.345E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.356E+02	0.544E+02
6	0.334E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.356E+02	0.535E+02
7	0.318E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.317E+02	0.465E+02
8	0.243E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.314E+02	0.414E+02
9	0.226E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.297E+02	0.384E+02
10	0.203E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.373E+02	0.468E+02
11	0.192E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.351E+02	0.434E+02
12	0.164E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.350E+02	0.418E+02
13	0.162E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.384E+02	0.458E+02
14	0.140E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.350E+02	0.407E+02

LAYER 11 FOR MONTH 18

1	0.959E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.147E+02	0.356E+03
2	0.873E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.594E+02	0.467E+03
3	0.638E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.239E+02	0.661E+02
4	0.532E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.531E+02	0.113E+03
5	0.452E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.550E+02	0.100E+03
6	0.440E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.448E+02	0.800E+02
7	0.411E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.559E+02	0.949E+02
8	0.352E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.571E+02	0.881E+02
9	0.334E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.497E+02	0.746E+02
10	0.301E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.488E+02	0.698E+02
11	0.248E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.577E+02	0.767E+02
12	0.234E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.589E+02	0.770E+02
13	0.212E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.566E+02	0.718E+02

LAYER 1 FOR MONTH 121

1	0.712E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.500E+02	0.174E+03
2	0.576E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.770E+02	0.181E+03
3	0.276E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.767E+02	0.106E+03
4	0.258E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.719E+02	0.970E+02
5	0.225E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.805E+02	0.104E+03
6	0.197E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.882E+02	0.110E+03
7	0.150E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.847E+02	0.996E+02
8	0.118E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.884E+02	0.100E+03
9	0.102E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.840E+02	0.935E+02

SENSITIVITY OF INPUTS ON ATOTAL

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 121								
1	0.725E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.285E+03	0.104E+04
2	0.678E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.263E+03	0.816E+03
3	0.567E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.366E+03	0.845E+03
4	0.360E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.408E+03	0.637E+03
5	0.324E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.398E+03	0.588E+03
6	0.293E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.354E+03	0.502E+03
7	0.291E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.340E+03	0.479E+03
8	0.278E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.366E+03	0.507E+03
9	0.265E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.350E+03	0.477E+03
10	0.243E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.357E+03	0.472E+03
11	0.212E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.371E+03	0.471E+03
12	0.176E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.371E+03	0.450E+03
13	0.166E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.404E+03	0.485E+03
14	0.146E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.352E+03	0.412E+03
15	0.110E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.403E+03	0.453E+03

LAYER 11 FOR MONTH 121								
1	0.749E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.566E+03	0.225E+04
2	0.679E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.742E+03	0.231E+04
3	0.533E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.528E+03	0.113E+04
4	0.475E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.976E+03	0.186E+04
5	0.466E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.744E+03	0.139E+04
6	0.407E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.127E+04	0.214E+04
7	0.400E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.125E+04	0.208E+04
8	0.351E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.122E+04	0.189E+04
9	0.335E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.126E+04	0.189E+04
10	0.332E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.127E+04	0.191E+04
11	0.325E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.132E+04	0.195E+04
12	0.271E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.118E+04	0.162E+04
13	0.244E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.102E+04	0.135E+04
14	0.241E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.113E+04	0.148E+04
15	0.214E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.115E+04	0.146E+04
16	0.196E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.124E+04	0.154E+04
17	0.146E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.137E+04	0.160E+04
18	0.122E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.140E+04	0.159E+04

LAYER 1 FOR MONTH 126								
1	0.706E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.510E+02	0.174E+03
2	0.560E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.798E+02	0.191E+03
3	0.278E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.784E+02	0.109E+03
4	0.265E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.731E+02	0.994E+02
5	0.226E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.824E+02	0.106E+03
6	0.196E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.904E+02	0.113E+03
7	0.146E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.870E+02	0.102E+03
8	0.117E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.906E+02	0.103E+03

LAYER 5 FOR MONTH 126								
1	0.725E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.290E+03	0.105E+04

SENSITIVITY OF INPUTS ON ATOTAL

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
2	0.678E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.265E+03	0.822E+03
3	0.565E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.369E+03	0.848E+03
4	0.359E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.411E+03	0.641E+03
5	0.321E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.401E+03	0.591E+03
6	0.291E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.342E+03	0.483E+03
6	0.291E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.358E+03	0.505E+03
7	0.279E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.368E+03	0.511E+03
8	0.265E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.353E+03	0.481E+03
9	0.241E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.361E+03	0.475E+03
10	0.218E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.371E+03	0.475E+03
11	0.174E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.374E+03	0.453E+03
12	0.166E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.408E+03	0.489E+03
13	0.148E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.354E+03	0.416E+03
14	0.113E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.406E+03	0.458E+03

LAYER 11 FOR MONTH 126

1	0.687E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.733E+03	0.234E+04
2	0.675E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.785E+03	0.241E+04
3	0.517E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.552E+03	0.114E+04
4	0.483E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.100E+04	0.194E+04
5	0.467E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.769E+03	0.144E+04
6	0.409E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.129E+04	0.219E+04
7	0.408E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.131E+04	0.221E+04
8	0.356E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.126E+04	0.196E+04
9	0.337E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.130E+04	0.196E+04
10	0.336E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.131E+04	0.198E+04
11	0.324E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.136E+04	0.201E+04
12	0.278E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.121E+04	0.168E+04
13	0.247E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.105E+04	0.140E+04
14	0.244E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.116E+04	0.153E+04
15	0.211E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.119E+04	0.151E+04
16	0.210E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.128E+04	0.162E+04
17	0.146E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.141E+04	0.165E+04
18	0.117E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.144E+04	0.164E+04

Table F.5.5
Sensitivity Analysis
on the Yearly Acid Flux

SENSITIVITY OF INPUTS ON AYEAR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.916E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.659E-02	0.786E-01
2	0.790E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.166E-01	0.791E-01
3	0.719E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.503E-01	0.179E+00
4	0.675E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.410E-01	0.126E+00
5	0.647E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.275E-01	0.781E-01
6	0.636E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.265E-01	0.727E-01
LAYER 5 FOR MONTH 13								
1	0.947E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.962E-01	0.180E+01
2	0.783E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.110E+00	0.505E+00
3	0.748E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.285E+00	0.113E+01
4	0.613E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.241E+00	0.623E+00
5	0.423E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.263E+00	0.456E+00
6	0.291E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.273E+00	0.385E+00
7	0.278E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.210E+00	0.291E+00
8	0.233E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.276E+00	0.360E+00
LAYER 11 FOR MONTH 13								
1	0.951E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.127E+00	0.257E+01
2	0.900E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.104E+00	0.104E+01
3	0.847E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.521E+00	0.340E+01
4	0.648E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.249E+00	0.707E+00
5	0.481E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.472E+00	0.909E+00
6	0.450E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.475E+00	0.864E+00
7	0.447E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.479E+00	0.866E+00
8	0.353E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.505E+00	0.780E+00
9	0.341E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.493E+00	0.748E+00
10	0.305E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.426E+00	0.613E+00
11	0.236E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.504E+00	0.660E+00
12	0.215E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.496E+00	0.631E+00
13	0.203E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.507E+00	0.636E+00
14	0.201E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.507E+00	0.635E+00
15	0.137E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.512E+00	0.594E+00
LAYER 1 FOR MONTH 18								
1	0.874E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.349E+01	0.278E+02
2	0.780E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.213E+01	0.966E+01
3	0.712E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.276E+01	0.960E+01
4	0.523E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.541E+01	0.114E+02
5	0.481E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.297E+01	0.573E+01
6	0.397E+00	-	EAI	0.100E+05	0.117E+05	0.256E+05	0.549E+01	0.910E+01
7	0.195E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.787E+01	0.977E+01
8	0.187E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.699E+01	0.860E+01
9	0.187E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.699E+01	0.860E+01
9	0.161E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.793E+01	0.944E+01
10	0.146E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.792E+01	0.927E+01
11	0.144E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.719E+01	0.840E+01
12	0.109E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.815E+01	0.915E+01



SENSITIVITY OF INPUTS ON AYEAR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 18								
1	0.920E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.259E+01	0.324E+02
2	0.551E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.776E+01	0.173E+02
3	0.526E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.597E+01	0.126E+02
4	0.453E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.809E+01	0.148E+02
5	0.380E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.827E+01	0.134E+02
6	0.360E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.706E+01	0.110E+02
7	0.356E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.816E+01	0.127E+02
8	0.283E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.663E+01	0.900E+01
9	0.169E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.795E+01	0.956E+01
LAYER 11 FOR MONTH 18								
1	0.978E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.713E+01	0.318E+03
2	0.887E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.284E+02	0.252E+03
3	0.580E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.177E+02	0.421E+02
4	0.510E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.148E+02	0.302E+02
5	0.475E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.258E+02	0.491E+02
6	0.451E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.209E+02	0.381E+02
7	0.432E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.261E+02	0.460E+02
8	0.354E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.271E+02	0.420E+02
8	0.354E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.275E+02	0.425E+02
9	0.320E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.274E+02	0.403E+02
10	0.309E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.231E+02	0.335E+02
11	0.264E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.278E+02	0.378E+02
12	0.217E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.269E+02	0.344E+02
13	0.202E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.276E+02	0.346E+02
14	0.146E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.279E+02	0.326E+02
15	0.126E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.279E+02	0.320E+02
LAYER 1 FOR MONTH 121								
1	0.979E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.160E-03	0.745E-02
2	0.599E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.356E-02	0.887E-02
3	0.426E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.533E-02	0.929E-02
4	0.404E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.402E-02	0.674E-02
5	0.393E+00	-	FALOM	0.100E-01	0.750E-01	0.600E+00	0.543E-02	0.894E-02
6	0.343E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.423E-02	0.644E-02
7	0.233E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.482E-02	0.629E-02
8	0.210E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.520E-02	0.658E-02
9	0.197E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.160E-03	0.199E-03
10	0.173E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.472E-02	0.571E-02
LAYER 5 FOR MONTH 121								
1	0.878E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.769E-01	0.629E+00
2	0.760E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.171E+00	0.714E+00
3	0.677E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.256E+00	0.793E+00
4	0.593E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.145E+00	0.357E+00
5	0.578E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.153E+00	0.362E+00
6	0.486E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.320E+00	0.623E+00
7	0.476E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.260E+00	0.497E+00

SENSITIVITY OF INPUTS ON AYEAR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
8	0.461E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.322E+00	0.598E+00
9	0.326E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.253E+00	0.376E+00
10	0.325E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.313E+00	0.463E+00
11	0.292E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.314E+00	0.443E+00
12	0.268E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.270E+00	0.369E+00
13	0.265E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.318E+00	0.433E+00

LAYER 11 FOR MONTH 121

1	0.844E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.532E-01	0.341E+00
2	0.806E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.308E+00	0.159E+01
3	0.651E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.658E+00	0.188E+01
4	0.629E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.743E+00	0.200E+01
5	0.594E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.761E+00	0.187E+01
6	0.551E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.825E+00	0.184E+01
7	0.518E+00	-	WT1	0.450E+00	0.500E+00	0.550E+00	0.782E+00	0.162E+01
8	0.515E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.758E+00	0.156E+01
9	0.514E+00	-	FALDH	0.100E-01	0.750E-01	0.600E+00	0.826E+00	0.170E+01
10	0.512E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.166E+01	0.340E+01
11	0.508E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.778E+00	0.158E+01
12	0.496E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.778E+00	0.154E+01
13	0.488E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.789E+00	0.154E+01
14	0.470E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.817E+00	0.154E+01
15	0.456E+00	+	XALDH3	0.140E-02	0.230E-02	0.320E-02	0.835E+00	0.154E+01
16	0.388E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.838E+00	0.137E+01
17	0.334E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.623E+00	0.935E+00
18	0.330E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.645E+00	0.963E+00
19	0.236E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.771E+00	0.101E+01
20	0.234E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.660E+00	0.862E+00
21	0.214E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.757E+00	0.963E+00
22	0.179E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.770E+00	0.938E+00
23	0.177E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.768E+00	0.934E+00
24	0.123E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.740E+00	0.843E+00

LAYER 1 FOR MONTH 126

1	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.396E-02	0.282E+01
2	0.996E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.396E-02	0.916E+00
3	0.523E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.116E+01	0.243E+01
4	0.354E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.174E+01	0.269E+01
5	0.313E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.173E+01	0.252E+01
6	0.264E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.191E+01	0.260E+01
7	0.167E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.230E+01	0.276E+01
8	0.165E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.188E+01	0.225E+01
9	0.157E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.219E+01	0.260E+01
10	0.105E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.211E+01	0.236E+01

LAYER 5 FOR MONTH 126

1	0.899E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.453E+00	0.447E+01
2	0.700E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.454E+01	0.152E+02
3	0.644E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.233E+01	0.654E+01
4	0.409E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.227E+01	0.385E+01

SENSITIVITY OF INPUTS ON AYEAR

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
5	0.384E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.333E+01	0.541E+01
6	0.361E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.262E+01	0.411E+01
7	0.334E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.292E+01	0.452E+01
8	0.337E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.337E+01	0.508E+01
9	0.292E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.354E+01	0.500E+01
10	0.225E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.366E+01	0.473E+01
11	0.220E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.305E+01	0.391E+01
12	0.207E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.315E+01	0.396E+01
13	0.193E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.352E+01	0.436E+01
14	0.177E+00	-	FALOW	0.100E-01	0.750E-01	0.600E+00	0.359E+01	0.436E+01
15	0.151E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.344E+01	0.405E+01
16	0.145E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.376E+01	0.440E+01

LAYER 11 FOR MONTH 126

1	0.679E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.271E+02	0.844E+02
2	0.599E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.421E+02	0.105E+03
3	0.574E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.434E+02	0.102E+03
4	0.478E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.255E+02	0.488E+02
4	0.478E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.889E+02	0.170E+03
5	0.471E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.430E+02	0.813E+02
6	0.467E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.131E+02	0.246E+02
7	0.458E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.415E+02	0.766E+02
8	0.449E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.323E+02	0.586E+02
9	0.436E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.409E+02	0.726E+02
10	0.427E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.418E+02	0.730E+02
11	0.417E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.399E+02	0.685E+02
12	0.333E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.346E+02	0.518E+02
13	0.333E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.434E+02	0.650E+02
14	0.321E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.356E+02	0.525E+02
15	0.278E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.424E+02	0.587E+02
16	0.276E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.433E+02	0.597E+02
17	0.245E+00	-	FALOW	0.100E-01	0.750E-01	0.600E+00	0.440E+02	0.582E+02
18	0.244E+00	-	WT1	0.450E+00	0.500E+00	0.550E+00	0.423E+02	0.560E+02
19	0.231E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.424E+02	0.551E+02
20	0.191E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.437E+02	0.540E+02
21	0.162E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.422E+02	0.504E+02
22	0.133E+00	+	IALON3	0.140E-02	0.230E-02	0.320E-02	0.455E+02	0.525E+02
23	0.126E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.427E+02	0.489E+02
24	0.123E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.407E+02	0.465E+02
25	0.111E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.430E+02	0.483E+02

Table F.5.6
Sensitivity Analysis
on Ca^{2+} Concentration

SENSITIVITY OF INPUTS ON Ca^{2+}

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.443E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.520E-02	0.933E-02
2	0.368E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.706E-02	0.112E-01
3	0.323E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.668E-02	0.987E-02
4	0.133E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.805E-02	0.929E-02
LAYER 5 FOR MONTH 13								
1	0.855E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.116E-02	0.802E-02
2	0.594E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.186E-02	0.457E-02
3	0.583E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.165E-02	0.396E-02
4	0.519E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.212E-02	0.440E-02
5	0.500E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.288E-02	0.577E-02
6	0.400E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.255E-02	0.425E-02
7	0.269E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.301E-02	0.412E-02
8	0.213E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.321E-02	0.408E-02
9	0.193E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.353E-02	0.437E-02
LAYER 11 FOR MONTH 13								
1	0.935E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.387E-03	0.591E-02
2	0.702E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.564E-03	0.189E-02
3	0.620E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.140E-02	0.370E-02
4	0.539E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.133E-02	0.289E-02
5	0.475E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.109E-02	0.208E-02
6	0.442E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.115E-02	0.207E-02
7	0.441E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.115E-02	0.205E-02
8	0.348E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.127E-02	0.195E-02
9	0.335E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.133E-02	0.200E-02
10	0.295E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.162E-02	0.229E-02
11	0.231E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.150E-02	0.195E-02
12	0.212E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.166E-02	0.211E-02
13	0.209E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.157E-02	0.199E-02
14	0.198E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.156E-02	0.194E-02
15	0.196E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.156E-02	0.194E-02
16	0.134E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.167E-02	0.192E-02
LAYER 1 FOR MONTH 18								
1	0.843E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.643E-03	0.409E-02
2	0.808E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.105E-02	0.545E-02
3	0.688E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.230E-02	0.737E-02
4	0.537E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.425E-02	0.918E-02
5	0.536E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.318E-02	0.686E-02
6	0.450E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.196E-02	0.356E-02
7	0.246E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.237E-02	0.314E-02
8	0.237E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.219E-02	0.288E-02
9	0.215E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.226E-02	0.288E-02
10	0.188E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.247E-02	0.305E-02
11	0.174E+00	-	UMAX	0.115E+02	0.130E+02	0.145E+02	0.235E-02	0.285E-02
12	0.131E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.239E-02	0.275E-02

SENSITIVITY OF INPUTS ON CA

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 18								
1	0.824E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.159E-02	0.902E-02
2	0.532E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.277E-02	0.592E-02
3	0.469E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.309E-02	0.581E-02
4	0.465E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.400E-02	0.747E-02
5	0.399E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.342E-02	0.569E-02
6	0.360E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.540E-02	0.843E-02
7	0.339E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.352E-02	0.532E-02
8	0.220E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.595E-02	0.763E-02
9	0.193E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.441E-02	0.547E-02
10	0.177E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.480E-02	0.583E-02
11	0.102E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.538E-02	0.600E-02
12	0.100E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.486E-02	0.540E-02

LAYER 11 FOR MONTH 18								
1	0.968E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.174E-03	0.550E-02
2	0.745E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.498E-03	0.195E-02
3	0.537E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.138E-02	0.297E-02
4	0.484E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.184E-02	0.357E-02
5	0.457E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.116E-02	0.213E-02
6	0.452E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.112E-02	0.205E-02
7	0.406E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.125E-02	0.210E-02
8	0.404E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.125E-02	0.210E-02
9	0.389E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.128E-02	0.209E-02
10	0.294E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.167E-02	0.236E-02
11	0.254E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.151E-02	0.202E-02
12	0.233E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.159E-02	0.207E-02
13	0.210E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.172E-02	0.218E-02
14	0.172E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.165E-02	0.200E-02
15	0.139E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.171E-02	0.199E-02

LAYER 1 FOR MONTH 121								
1	0.322E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.906E-02	0.134E-01
2	0.212E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.975E-02	0.124E-01
3	0.208E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.979E-02	0.124E-01
4	0.133E+00	-	FALON	0.100E-01	0.750E-01	0.600E+00	0.107E-01	0.124E-01
5	0.122E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.107E-01	0.122E-01
6	0.101E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.100E-01	0.112E-01

LAYER 5 FOR MONTH 121								
1	0.581E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.271E-02	0.647E-02
2	0.471E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.447E-02	0.944E-02
3	0.470E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.385E-02	0.727E-02
4	0.405E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.434E-02	0.729E-02
5	0.387E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.414E-02	0.675E-02
6	0.236E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.591E-02	0.773E-02
7	0.158E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.598E-02	0.710E-02
8	0.155E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.575E-02	0.680E-02
9	0.115E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.514E-02	0.581E-02

SENSITIVITY OF INPUTS ON CA

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
10	0.106E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.583E-02	0.652E-02
10	0.106E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.581E-02	0.650E-02
11	0.101E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.583E-02	0.649E-02

LAYER 11 FOR MONTH 121

1	0.858E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.291E-03	0.205E-02
2	0.840E+00	-	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.542E-03	0.338E-02
3	0.826E+00	+	FALON	0.100E-01	0.750E-01	0.600E+00	0.585E-03	0.337E-02
4	0.677E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.829E-03	0.256E-02
5	0.651E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.282E-02	0.809E-02
6	0.610E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.881E-03	0.226E-02
7	0.570E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.948E-03	0.220E-02
8	0.544E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.976E-03	0.214E-02
9	0.534E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.100E-02	0.215E-02
10	0.511E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.103E-02	0.215E-02
11	0.515E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.113E-02	0.232E-02
12	0.514E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.103E-02	0.212E-02
13	0.511E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.103E-02	0.211E-02
14	0.508E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.153E-02	0.311E-02
15	0.495E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.103E-02	0.204E-02
16	0.482E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.104E-02	0.200E-02
17	0.347E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.177E-02	0.271E-02
18	0.245E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.197E-02	0.262E-02
19	0.207E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.158E-02	0.199E-02
20	0.201E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.190E-02	0.237E-02
21	0.147E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.193E-02	0.226E-02
22	0.136E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.188E-02	0.217E-02
23	0.129E+00	-	UNAX	0.115E+02	0.130E+02	0.145E+02	0.198E-02	0.227E-02
24	0.109E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.197E-02	0.221E-02

LAYER 1 FOR MONTH 126

1	0.361E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.668E-02	0.105E-01
2	0.357E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.549E-02	0.855E-02
3	0.245E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.732E-02	0.997E-02
4	0.226E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.771E-02	0.997E-02
5	0.196E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.661E-02	0.822E-02
6	0.161E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.737E-02	0.878E-02

LAYER 5 FOR MONTH 126

1	0.404E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.463E-02	0.778E-02
2	0.375E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.627E-02	0.100E-01
3	0.346E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.653E-02	0.999E-02
4	0.311E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.600E-02	0.870E-02
5	0.292E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.568E-02	0.801E-02
6	0.251E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.621E-02	0.829E-02
7	0.237E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.437E-02	0.572E-02
8	0.174E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.697E-02	0.844E-02
9	0.147E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.672E-02	0.788E-02
10	0.142E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.741E-02	0.864E-02

SENSITIVITY OF INPUTS ON CA

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 11 FOR MONTH 126								
1	0.750E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.672E-03	0.269E-02
1	0.750E+00	-	ME1	-0.500E-01	-0.500E+00	-0.150E+01	0.129E-02	0.518E-02
2	0.730E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.108E-02	0.399E-02
3	0.508E+00	+	EAL	0.100E+05	0.117E+05	0.256E+05	0.199E-02	0.405E-02
4	0.495E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.120E-02	0.238E-02
5	0.486E+00	-	KFEEDH	0.127E+01	0.398E+02	0.127E+04	0.144E-02	0.280E-02
6	0.482E+00	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.211E-02	0.407E-02
7	0.473E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.177E-02	0.336E-02
8	0.411E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.139E-02	0.236E-02
9	0.386E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.192E-02	0.312E-02
10	0.377E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.162E-02	0.260E-02
11	0.355E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.165E-02	0.256E-02
12	0.351E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.164E-02	0.253E-02
13	0.339E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.193E-02	0.293E-02
14	0.291E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.179E-02	0.252E-02
15	0.200E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.210E-02	0.262E-02
16	0.195E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.193E-02	0.239E-02
17	0.165E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.201E-02	0.241E-02
18	0.138E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.206E-02	0.239E-02
18	0.126E+00	-	UMAX	0.115E+02	0.130E+02	0.145E+02	0.219E-02	0.251E-02

Table F.5.7
Sensitivity Analysis
on Total Calcium Concentration

SENSITIVITY OF INPUTS ON CAT

	RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13									
	1	0.242E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.129E-01	0.171E-01
	2	0.217E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.148E-01	0.189E-01
	3	0.181E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.144E-01	0.176E-01
	4	0.176E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.148E-01	0.180E-01
LAYER 5 FOR MONTH 13									
	1	0.435E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.891E-02	0.158E-01
	2	0.220E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.961E-02	0.123E-01
	3	0.213E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.106E-01	0.135E-01
	4	0.212E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.103E-01	0.131E-01
	5	0.197E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.940E-02	0.117E-01
	6	0.188E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.987E-02	0.121E-01
	7	0.142E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.103E-01	0.120E-01
LAYER 11 FOR MONTH 13									
	1	0.404E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.813E-02	0.137E-01
	2	0.220E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.843E-02	0.108E-01
	3	0.200E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.915E-02	0.114E-01
	4	0.146E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.908E-02	0.106E-01
	5	0.138E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.831E-02	0.964E-02
	6	0.101E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.884E-02	0.983E-02
LAYER 1 FOR MONTH 18									
	1	0.335E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.101E-01	0.151E-01
	2	0.333E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.880E-02	0.132E-01
	3	0.291E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.120E-01	0.169E-01
	3	0.291E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.839E-02	0.118E-01
	4	0.252E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.109E-01	0.146E-01
	5	0.220E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.903E-02	0.116E-01
	6	0.142E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.971E-02	0.113E-01
LAYER 5 FOR MONTH 18									
	1	0.443E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.933E-02	0.168E-01
	2	0.231E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.105E-01	0.137E-01
	3	0.228E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.117E-01	0.152E-01
	4	0.204E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.116E-01	0.145E-01
	5	0.201E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.108E-01	0.136E-01
	6	0.188E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.131E-01	0.162E-01
	7	0.169E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.112E-01	0.134E-01
	8	0.138E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.113E-01	0.131E-01
	9	0.109E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.137E-01	0.154E-01
LAYER 11 FOR MONTH 18									
	1	0.402E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.792E-02	0.133E-01
	2	0.220E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.849E-02	0.109E-01
	3	0.153E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.959E-02	0.113E-01
	4	0.150E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.825E-02	0.970E-02
	5	0.149E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.913E-02	0.107E-01

SENSITIVITY OF INPUTS ON CAT

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 121								
1	0.204E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.168E-01	0.211E-01
2	0.130E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.175E-01	0.201E-01
3	0.128E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.175E-01	0.201E-01
4	0.114E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.169E-01	0.191E-01
LAYER 5 FOR MONTH 121								
1	0.265E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.105E-01	0.142E-01
2	0.245E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.122E-01	0.162E-01
3	0.228E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.116E-01	0.150E-01
4	0.196E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.121E-01	0.150E-01
5	0.180E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.119E-01	0.145E-01
6	0.167E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.126E-01	0.151E-01
7	0.118E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.137E-01	0.155E-01
LAYER 11 FOR MONTH 121								
1	0.333E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.106E-01	0.158E-01
2	0.255E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.829E-02	0.111E-01
3	0.251E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.833E-02	0.111E-01
4	0.217E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.866E-02	0.111E-01
5	0.179E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.804E-02	0.980E-02
6	0.168E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.858E-02	0.103E-01
7	0.145E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.928E-02	0.109E-01
8	0.138E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.863E-02	0.100E-01
9	0.126E+00	+	V8	0.600E-02	0.300E-01	0.400E-01	0.870E-02	0.995E-02
10	0.119E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.887E-02	0.101E-01
11	0.118E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.872E-02	0.989E-02
12	0.116E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.875E-02	0.990E-02
13	0.113E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.878E-02	0.990E-02
14	0.110E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.878E-02	0.987E-02
15	0.109E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.878E-02	0.985E-02
16	0.103E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.878E-02	0.979E-02
LAYER 1 FOR MONTH 126								
1	0.207E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.144E-01	0.182E-01
2	0.191E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.141E-01	0.175E-01
3	0.187E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.132E-01	0.163E-01
4	0.138E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.153E-01	0.177E-01
5	0.127E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.155E-01	0.177E-01
6	0.101E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.144E-01	0.160E-01
LAYER 5 FOR MONTH 126								
1	0.211E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.140E-01	0.178E-01
2	0.202E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.124E-01	0.155E-01
3	0.199E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.137E-01	0.171E-01
4	0.195E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.143E-01	0.177E-01
5	0.164E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.137E-01	0.164E-01
6	0.148E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.134E-01	0.158E-01
7	0.130E+00	-	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.140E-01	0.160E-01

SENSITIVITY OF INPUTS ON CAT

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
8	0.101E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.121E-01	0.135E-01

LAYER 11 FOR MONTH 126

1	0.301E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.904E-02	0.129E-01
2	0.248E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.883E-02	0.117E-01
3	0.217E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.886E-02	0.113E-01
4	0.193E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.842E-02	0.104E-01
5	0.174E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.974E-02	0.118E-01
6	0.166E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.985E-02	0.118E-01
7	0.143E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.952E-02	0.111E-01
8	0.129E+00	-	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.919E-02	0.106E-01
9	0.116E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.895E-02	0.101E-01
10	0.111E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.966E-02	0.109E-01



Table F.5.8
Sensitivity Analysis
on Fe^{2+} Concentration

SENSITIVITY OF INPUTS ON Fe^{2+}

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 13								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.100E-07	0.181E-02
LAYER 11 FOR MONTH 13								
1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.100E-07	0.585E-02
2	0.985E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.142E-02	0.934E-01
3	0.834E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.367E-02	0.222E-01
4	0.336E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.468E-02	0.704E-02
5	0.320E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.540E-02	0.794E-02
6	0.316E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.325E-02	0.476E-02
7	0.189E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.570E-02	0.703E-02
8	0.162E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.572E-02	0.682E-02
9	0.119E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.550E-02	0.624E-02
10	0.116E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.580E-02	0.656E-02
LAYER 5 FOR MONTH 18								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.100E-07	0.131E-02
LAYER 11 FOR MONTH 18								
1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.100E-07	0.154E-02
2	0.997E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.418E-03	0.122E+00
3	0.462E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.139E-02	0.259E-02
4	0.440E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.111E-02	0.199E-02
5	0.424E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.143E-02	0.248E-02
6	0.375E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.180E-02	0.288E-02
7	0.335E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.140E-02	0.211E-02
8	0.328E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.145E-02	0.215E-02
9	0.283E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.146E-02	0.204E-02
10	0.244E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.147E-02	0.195E-02
11	0.235E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.135E-02	0.177E-02
12	0.220E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.138E-02	0.176E-02
13	0.145E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.152E-02	0.178E-02
14	0.121E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.139E-02	0.158E-02
LAYER 5 FOR MONTH 121								
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.100E-07	0.195E-02
LAYER 11 FOR MONTH 121								
1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.100E-07	0.627E-01
2	0.957E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.701E-02	0.164E+00
3	0.912E+00	+	XALDH3	0.140E-02	0.230E-02	0.320E-02	0.715E-02	0.811E-01
4	0.909E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.825E-02	0.907E-01
5	0.856E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.986E-02	0.683E-01
6	0.820E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.127E-01	0.705E-01
7	0.811E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.129E-01	0.680E-01
8	0.790E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.126E-01	0.599E-01
9	0.763E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.131E-01	0.552E-01
10	0.762E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.131E-01	0.549E-01
11	0.757E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.134E-01	0.552E-01

SENSITIVITY OF INPUTS ON FE2

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
12	0.756E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.134E-01	0.550E-01
13	0.751E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.138E-01	0.554E-01
14	0.659E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.272E-01	0.797E-01
15	0.584E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.232E-01	0.556E-01
16	0.579E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.131E-01	0.310E-01
17	0.575E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.398E-01	0.938E-01
18	0.574E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.235E-01	0.552E-01
19	0.522E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.263E-01	0.551E-01
20	0.391E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.121E-01	0.199E-01
21	0.277E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.133E-01	0.184E-01
22	0.275E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.274E-01	0.378E-01
23	0.242E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.113E-01	0.149E-01
24	0.218E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.206E-01	0.263E-01
25	0.188E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.133E-01	0.163E-01
26	0.149E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.277E-01	0.326E-01

LAYER 5 FOR MONTH 126

1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.100E-07	0.195E-02
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LAYER 11 FOR MONTH 126

1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.100E-07	0.525E-02
2	0.957E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.701E-02	0.164E+00
3	0.912E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.715E-02	0.811E-01
4	0.891E+00	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.568E-02	0.522E-01
5	0.856E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.986E-02	0.683E-01
6	0.820E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.127E-01	0.705E-01
7	0.811E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.129E-01	0.680E-01
8	0.790E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.126E-01	0.599E-01
9	0.763E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.215E-01	0.907E-01
9	0.763E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.131E-01	0.552E-01
10	0.762E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.131E-01	0.549E-01
11	0.757E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.134E-01	0.552E-01
12	0.756E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.134E-01	0.550E-01
13	0.751E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.138E-01	0.554E-01
14	0.659E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.272E-01	0.797E-01
15	0.584E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.232E-01	0.556E-01
16	0.579E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.131E-01	0.310E-01
17	0.574E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.235E-01	0.552E-01
18	0.522E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.263E-01	0.551E-01
19	0.391E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.121E-01	0.199E-01
20	0.337E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.398E-01	0.601E-01
21	0.277E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.133E-01	0.184E-01
22	0.275E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.274E-01	0.378E-01
23	0.242E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.113E-01	0.149E-01
24	0.218E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.206E-01	0.263E-01
25	0.188E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.133E-01	0.163E-01
26	0.149E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.277E-01	0.326E-01

Table F.5.9
Sensitivity Analysis
on Total Iron II Concentration

SENSITIVITY OF INPUTS ON FE2T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.999E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.395E-05	0.464E-02
2	0.821E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.608E-04	0.340E-03
3	0.338E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.939E-04	0.146E-03
4	0.335E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.676E-04	0.105E-03
5	0.304E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.652E-04	0.937E-04
6	0.269E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.592E-04	0.811E-04
7	0.115E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.889E-04	0.100E-03
8	0.102E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.894E-04	0.996E-04
LAYER 5 FOR MONTH 13								
1	0.998E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.652E-04	0.309E-01
2	0.972E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.611E-03	0.218E-01
3	0.720E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.505E-03	0.181E-02
4	0.685E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.483E-03	0.153E-02
5	0.473E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.550E-03	0.104E-02
6	0.469E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.434E-03	0.818E-03
7	0.352E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.564E-03	0.871E-03
8	0.238E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.537E-03	0.706E-03
9	0.233E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.543E-03	0.707E-03
10	0.139E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.599E-03	0.696E-03
11	0.111E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.558E-03	0.628E-03
LAYER 11 FOR MONTH 13								
1	0.985E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.142E-02	0.934E-01
2	0.931E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.585E-02	0.848E-01
3	0.834E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.367E-02	0.222E-01
4	0.336E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.468E-02	0.704E-02
5	0.320E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.540E-02	0.794E-02
6	0.316E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.325E-02	0.476E-02
7	0.189E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.570E-02	0.703E-02
8	0.162E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.572E-02	0.682E-02
9	0.119E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.550E-02	0.624E-02
10	0.116E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.580E-02	0.656E-02
LAYER 1 FOR MONTH 18								
1	0.997E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.905E-05	0.278E-02
2	0.988E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.177E-03	0.143E-01
3	0.979E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.424E-04	0.199E-02
4	0.965E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.569E-04	0.161E-02
5	0.880E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.455E-03	0.379E-02
6	0.822E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.440E-03	0.247E-02
7	0.491E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.589E-03	0.116E-02
8	0.487E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.509E-03	0.991E-03
9	0.366E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.534E-03	0.843E-03
10	0.355E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.800E-03	0.124E-02
11	0.219E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.702E-03	0.899E-03



SENSITIVITY OF INPUTS ON FE2T

	RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 18									
	1	0.997E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.502E-04	0.199E-01
	2	0.915E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.440E-03	0.518E-02
	3	0.757E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.317E-03	0.131E-02
	4	0.571E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.425E-03	0.992E-03
	5	0.545E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.395E-03	0.867E-03
	6	0.509E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.328E-03	0.667E-03
	7	0.502E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.401E-03	0.805E-03
	8	0.378E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.421E-03	0.677E-03
	9	0.275E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.407E-03	0.561E-03
	10	0.207E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.407E-03	0.514E-03
	11	0.166E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.438E-03	0.525E-03
	12	0.123E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.445E-03	0.507E-03
LAYER 11 FOR MONTH 18									
	1	0.997E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.418E-03	0.122E+00
	2	0.980E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.154E-02	0.773E-01
	3	0.462E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.139E-02	0.259E-02
	4	0.440E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.111E-02	0.199E-02
	5	0.424E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.143E-02	0.248E-02
	6	0.375E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.180E-02	0.288E-02
	7	0.335E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.140E-02	0.211E-02
	8	0.328E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.145E-02	0.215E-02
	9	0.283E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.146E-02	0.204E-02
	10	0.244E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.147E-02	0.195E-02
	11	0.235E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.135E-02	0.177E-02
	12	0.220E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.138E-02	0.176E-02
	13	0.145E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.152E-02	0.178E-02
	14	0.121E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.139E-02	0.158E-02
LAYER 1 FOR MONTH 121									
	1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.334E-04
	1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.786E-05
	2	0.921E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.180E-04	0.227E-03
	3	0.807E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.161E-04	0.833E-04
	4	0.495E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.175E-04	0.346E-04
	5	0.434E+00	+	KFEEDH	0.127E+01	0.398E+02	0.127E+04	0.199E-04	0.351E-04
	6	0.374E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.244E-04	0.391E-04
	7	0.330E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.177E-04	0.273E-04
	8	0.330E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.253E-04	0.377E-04
	9	0.313E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.243E-04	0.354E-04
	10	0.181E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.229E-04	0.279E-04
	11	0.143E+00	-	YALOH3	0.140E-02	0.230E-02	0.320E-02	0.232E-04	0.270E-04
	12	0.122E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.235E-04	0.267E-04

SENSITIVITY OF INPUTS ON FE2T

	RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 121									
	1	0.923E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.575E-03	0.747E-02
	2	0.840E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.253E-03	0.158E-02
	3	0.824E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.630E-03	0.359E-02
	4	0.791E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.116E-02	0.553E-02
	5	0.695E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.886E-03	0.291E-02
	6	0.638E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.678E-03	0.188E-02
	7	0.584E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.113E-02	0.271E-02
	8	0.472E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.857E-03	0.162E-02
	9	0.328E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.100E-02	0.149E-02
	10	0.159E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.109E-02	0.130E-02
	11	0.121E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.112E-02	0.128E-02
	12	0.102E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.113E-02	0.126E-02

LAYER 11 FOR MONTH 121

1	0.877E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.828E-02	0.671E-01
2	0.755E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.202E-02	0.825E-02
3	0.738E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.165E-01	0.627E-01
4	0.734E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.145E-01	0.544E-01
5	0.731E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.141E-01	0.524E-01
6	0.726E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.140E-01	0.509E-01
7	0.721E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.141E-01	0.507E-01
8	0.720E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.141E-01	0.505E-01
9	0.720E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.141E-01	0.505E-01
9	0.716E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.144E-01	0.507E-01
10	0.712E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.151E-01	0.526E-01
11	0.710E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.162E-01	0.559E-01
12	0.708E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.148E-01	0.505E-01
13	0.692E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.289E-01	0.938E-01
14	0.690E+00	+	IALOH3	0.140E-02	0.230E-02	0.320E-02	0.158E-01	0.508E-01
15	0.375E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.118E-01	0.189E-01
16	0.369E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.116E-01	0.183E-01
17	0.352E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.122E-01	0.188E-01
18	0.324E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.338E-01	0.500E-01
19	0.164E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.132E-01	0.158E-01

LAYER 1 FOR MONTH 126

1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.000E+00	0.805E-04
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.000E+00	0.240E-03
2	0.900E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.115E-03	0.115E-02
3	0.673E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.908E-04	0.278E-03
4	0.656E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.112E-03	0.326E-03
5	0.634E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.677E-04	0.185E-03
6	0.433E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.902E-04	0.159E-03
7	0.397E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.720E-04	0.119E-03
8	0.381E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.924E-04	0.149E-03
9	0.319E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.110E-03	0.162E-03
10	0.190E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.108E-03	0.134E-03
11	0.140E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.107E-03	0.125E-03
12	0.139E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.112E-03	0.130E-03

SENSITIVITY OF INPUTS ON FE2T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 126								
1	0.954E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.211E-03	0.459E-02
2	0.894E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.264E-03	0.249E-02
3	0.709E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.338E-03	0.116E-02
4	0.651E+00	-	EAI	0.100E+05	0.117E+05	0.256E+05	0.252E-03	0.721E-03
5	0.616E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.361E-03	0.939E-03
6	0.599E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.623E-03	0.155E-02
7	0.547E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.515E-03	0.114E-02
8	0.422E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.496E-03	0.858E-03
9	0.410E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.450E-03	0.762E-03
10	0.199E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.548E-03	0.684E-03
11	0.188E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.206E-02	0.254E-02
12	0.173E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.568E-03	0.686E-03
13	0.120E+00	-	IALDH3	0.140E-02	0.230E-02	0.320E-02	0.590E-03	0.670E-03
LAYER 11 FOR MONTH 126								
1	0.824E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.379E-02	0.215E-01
2	0.774E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.386E-02	0.171E-01
3	0.770E+00	-	EAI	0.100E+05	0.117E+05	0.256E+05	0.106E-02	0.461E-02
4	0.751E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.123E-01	0.492E-01
5	0.694E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.348E-02	0.114E-01
6	0.644E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.367E-02	0.103E-01
7	0.595E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.217E-02	0.536E-02
8	0.457E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.261E-02	0.481E-02
9	0.447E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.337E-02	0.610E-02
10	0.436E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.343E-02	0.608E-02
11	0.433E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.320E-02	0.565E-02
12	0.416E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.316E-02	0.541E-02
13	0.377E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.374E-02	0.600E-02
14	0.327E+00	-	FALDH	0.100E-01	0.750E-01	0.600E+00	0.383E-02	0.568E-02
15	0.322E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.360E-02	0.531E-02
16	0.286E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.302E-02	0.423E-02
17	0.271E+00	+	IALDH3	0.140E-02	0.230E-02	0.320E-02	0.377E-02	0.517E-02
18	0.179E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.318E-02	0.388E-02
19	0.153E+00	+	IKFE3	0.500E-02	0.100E-01	0.500E-01	0.348E-02	0.411E-02
20	0.102E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.314E-02	0.350E-02

Table F.5.10
Sensitivity Analysis
on Fe³⁺ Concentration

SENSITIVITY OF INPUTS ON FE3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.100E+01	+	IP	0.320E-03	0.160E-02	0.780E-02	0.265E-16	0.703E-10
1	0.100E+01	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.276E-16	0.140E-09
1	0.100E+01	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.267E-16	0.140E-09
1	0.100E+01	+	KCONST	0.118E+04	0.230E+07	0.472E+08	0.321E-16	0.198E-03
2	0.999E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.847E-18	0.847E-15
3	0.998E+00	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.266E-16	0.177E-13
4	0.584E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.123E-16	0.295E-16
5	0.341E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.217E-16	0.329E-16
6	0.192E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.237E-16	0.293E-16
7	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.243E-16	0.297E-16
LAYER 5 FOR MONTH 13								
1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.783E-17	0.443E-08
1	0.100E+01	+	KCONST	0.118E+04	0.230E+07	0.472E+08	0.225E-16	0.626E-08
2	0.999E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.250E-18	0.250E-15
3	0.836E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.125E-17	0.762E-17
4	0.741E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.251E-17	0.970E-17
5	0.666E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.306E-17	0.916E-17
6	0.535E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.404E-17	0.868E-17
7	0.375E+00	+	V10	0.100E-01	0.500E-01	0.100E+00	0.518E-17	0.830E-17
8	0.349E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.639E-17	0.982E-17
9	0.338E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.640E-17	0.966E-17
10	0.302E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.570E-17	0.818E-17
11	0.275E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.658E-17	0.907E-17
12	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.715E-17	0.874E-17
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.778E-18	0.626E-08
2	0.999E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.248E-19	0.248E-16
3	0.998E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.741E-20	0.353E-17
4	0.997E+00	-	KCONST	0.118E+04	0.230E+07	0.472E+08	0.357E-20	0.130E-17
5	0.861E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.139E-18	0.100E-17
6	0.616E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.457E-18	0.119E-17
7	0.473E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.567E-18	0.108E-17
8	0.293E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.644E-18	0.911E-18
9	0.255E+00	-	IP	0.320E-03	0.160E-02	0.780E-02	0.611E-18	0.819E-18
10	0.240E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.677E-18	0.891E-18
11	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.710E-18	0.868E-18
12	0.180E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.864E-18	0.105E-17
13	0.161E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.713E-18	0.850E-18
14	0.146E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.676E-18	0.791E-18
15	0.121E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.694E-18	0.789E-18
LAYER 1 FOR MONTH 18								
1	0.100E+01	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.175E-16	0.443E-08
1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.157E-16	0.314E-08
1	0.100E+01	+	KCONST	0.118E+04	0.230E+07	0.472E+08	0.242E-16	0.157E-02
2	0.999E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.141E-09	0.141E-06

SENSITIVITY OF INPUTS ON FE3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
3	0.822E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.157E-08	0.885E-08
3	0.822E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.222E-08	0.125E-07
4	0.749E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.222E-08	0.885E-08
5	0.499E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.314E-08	0.626E-08
6	0.292E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.314E-08	0.443E-08
6	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.443E-08	0.626E-08
7	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.405E-08	0.495E-08

LAYER 5 FOR MONTH 18

1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.112E-16	0.314E-08
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.247E-16	0.443E-08
2	0.999E+00	+	KFED00	0.127E+01	0.398E+02	0.127E+04	0.358E-18	0.358E-15
3	0.878E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.132E-17	0.108E-16
4	0.680E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.420E-17	0.131E-16
5	0.613E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.493E-17	0.128E-16
6	0.534E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.576E-17	0.124E-16
7	0.488E+00	+	XP	0.320E-03	0.160E-02	0.790E-02	0.114E-16	0.223E-16
8	0.341E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.914E-17	0.139E-16
9	0.311E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.132E-16	0.192E-16
10	0.280E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.956E-17	0.133E-16
11	0.276E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.843E-17	0.116E-16
12	0.253E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.957E-17	0.128E-16
13	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.102E-16	0.125E-16
14	0.149E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.114E-16	0.134E-16
15	0.147E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.974E-17	0.114E-16

LAYER 11 FOR MONTH 18

1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.129E-17	0.885E-08
2	0.999E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.166E-20	0.147E-17
2	0.999E+00	+	KFED00	0.127E+01	0.398E+02	0.127E+04	0.410E-19	0.410E-16
3	0.998E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.132E-19	0.587E-17
4	0.613E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.759E-18	0.196E-17
5	0.471E+00	-	KCAC03	0.389E-08	0.448E-08	0.513E-08	0.939E-18	0.178E-17
6	0.247E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.110E-17	0.146E-17
7	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.117E-17	0.144E-17
8	0.134E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.113E-17	0.131E-17
9	0.116E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.115E-17	0.130E-17
10	0.114E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.110E-17	0.124E-17

LAYER 1 FOR MONTH 121

1	0.100E+01	-	XP	0.320E-03	0.160E-02	0.780E-02	0.497E-16	0.111E-11
1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.352E-07	0.198E-03
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.177E-10	0.198E-03
2	0.999E+00	-	YALOH3	0.140E-02	0.230E-02	0.320E-02	0.352E-07	0.249E-04
2	0.999E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.352E-07	0.249E-04
2	0.999E+00	-	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.352E-07	0.249E-04
3	0.998E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.498E-07	0.249E-04
3	0.998E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.498E-07	0.249E-04
3	0.998E+00	+	KFED00	0.127E+01	0.398E+02	0.127E+04	0.795E-06	0.399E-03
4	0.997E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.498E-07	0.177E-04



SENSITIVITY OF INPUTS ON FE3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
4	0.997E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.498E-07	0.177E-04
5	0.994E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.993E-07	0.177E-04
5	0.994E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.703E-07	0.125E-04
6	0.989E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.558E-06	0.498E-04
7	0.911E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.177E-04	0.198E-03
7	0.911E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.789E-06	0.885E-05
7	0.911E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.157E-05	0.177E-04
8	0.749E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.497E-16	0.198E-15
9	0.292E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.177E-04	0.249E-04
9	0.292E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.177E-04	0.249E-04
9	0.292E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.177E-04	0.249E-04
9	0.292E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.177E-04	0.249E-04
9	0.292E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.177E-04	0.249E-04
9	0.292E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.177E-04	0.249E-04
10	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.161E-04	0.197E-04

LAYER 5 FOR MONTH 121

1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.157E-08	0.111E-02
1	0.100E+01	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.157E-08	0.788E-03
2	0.874E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.141E-03	0.112E-02
3	0.822E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.198E-03	0.111E-02
3	0.822E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.140E-03	0.788E-03
4	0.645E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.280E-03	0.788E-03
4	0.645E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.558E-03	0.157E-02
5	0.499E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.558E-03	0.111E-02
5	0.499E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.558E-03	0.111E-02
6	0.292E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.558E-03	0.788E-03
6	0.292E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.558E-03	0.788E-03
6	0.292E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.558E-03	0.788E-03
6	0.292E+00	+	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.558E-03	0.788E-03
6	0.292E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.558E-03	0.788E-03
6	0.292E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.558E-03	0.788E-03
6	0.292E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.558E-03	0.788E-03
6	0.292E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.558E-03	0.788E-03
6	0.292E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.558E-03	0.788E-03
6	0.292E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.558E-03	0.788E-03
6	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.558E-03	0.788E-03
6	0.292E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.558E-03	0.788E-03
6	0.292E+00	-	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.558E-03	0.788E-03
7	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.720E-03	0.880E-03

LAYER 11 FOR MONTH 121

1	0.100E+01	-	ICACD3	0.000E+00	0.500E-03	0.100E-02	0.109E-17	0.111E-02
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.353E-20	0.157E-02
1	0.100E+01	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.149E-19	0.111E-02
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.587E-18	0.198E-09
2	0.999E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.100E-09	0.141E-06
3	0.749E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.157E-08	0.626E-08
4	0.499E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.314E-08	0.626E-08
5	0.292E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.222E-08	0.314E-08

SENSITIVITY OF INPUTS ON FE3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
5	0.292E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.314E-08	0.443E-08
5	0.292E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.314E-08	0.443E-08
5	0.292E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.314E-08	0.443E-08
5	0.292E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.314E-08	0.443E-08
5	0.292E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.314E-08	0.443E-08
5	0.292E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.314E-08	0.443E-08
5	0.292E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.314E-08	0.443E-08
5	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.314E-08	0.443E-08
6	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.287E-08	0.351E-08

LAYER 1 FOR MONTH 126

1	0.100E+01	-	IP	0.320E-03	0.160E-02	0.780E-02	0.497E-16	0.788E-09
1	0.100E+01	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.497E-16	0.198E-03
2	0.978E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.126E-04	0.563E-03
3	0.911E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.993E-04	0.111E-02
4	0.499E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.993E-04	0.198E-03
5	0.292E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.993E-04	0.140E-03
5	0.292E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.140E-03	0.198E-03
5	0.292E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.140E-03	0.198E-03
5	0.292E+00	+	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.140E-03	0.198E-03
5	0.292E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.140E-03	0.198E-03
5	0.292E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.140E-03	0.198E-03
5	0.292E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.140E-03	0.198E-03
5	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.140E-03	0.198E-03
5	0.292E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.140E-03	0.198E-03
5	0.292E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.140E-03	0.198E-03
6	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.128E-03	0.157E-03

LAYER 5 FOR MONTH 126

1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.222E-08	0.788E-03
1	0.100E+01	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.788E-09	0.280E-03
2	0.999E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.198E-06	0.140E-03
3	0.984E+00	+	KFE00H	0.127E+01	0.398E+02	0.127E+04	0.893E-05	0.563E-03
4	0.911E+00	+	IP	0.320E-03	0.160E-02	0.780E-02	0.703E-04	0.788E-03
5	0.822E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.140E-03	0.788E-03
6	0.645E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.993E-04	0.280E-03
7	0.499E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.140E-03	0.280E-03
7	0.499E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.140E-03	0.280E-03
7	0.499E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.198E-03	0.395E-03
7	0.499E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.198E-03	0.395E-03
8	0.292E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.198E-03	0.280E-03
8	0.292E+00	-	IALOH3	0.140E-02	0.230E-02	0.320E-02	0.198E-03	0.280E-03
8	0.292E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.280E-03	0.395E-03
8	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.198E-03	0.280E-03
9	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.256E-03	0.312E-03

LAYER 11 FOR MONTH 126

1	0.100E+01	-	ICAC03	0.000E+00	0.500E-03	0.100E-02	0.443E-08	0.157E-02
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.626E-08	0.222E-02
1	0.100E+01	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.785E-18	0.157E-02

SENSITIVITY OF INPUTS ON FE3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
1	0.100E+01	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.148E-18	0.111E-08
2	0.999E+00	+	KFEEDH	0.127E+01	0.398E+02	0.127E+04	0.100E-09	0.200E-06
3	0.645E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.314E-08	0.885E-08
4	0.499E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.222E-08	0.443E-08
4	0.499E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.443E-08	0.885E-08
5	0.292E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.443E-08	0.626E-08
5	0.292E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.443E-08	0.626E-08
5	0.292E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.443E-08	0.626E-08
5	0.292E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.443E-08	0.626E-08
5	0.292E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.443E-08	0.626E-08
5	0.292E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.443E-08	0.626E-08
5	0.292E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.443E-08	0.626E-08
6	0.182E+00	-	F3	0.180E+00	0.201E+00	0.220E+00	0.405E-08	0.495E-08

Table F.5.11
Sensitivity Analysis
on Total Iron III Concentration

SENSITIVITY OF INPUTS ON FE3T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.953E-10	0.323E-02
2	0.999E+00	+	KFEODM	0.127E+01	0.398E+02	0.127E+04	0.293E-11	0.293E-08
3	0.994E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.925E-10	0.148E-07
3	0.994E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.919E-10	0.148E-07
4	0.991E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.918E-10	0.106E-07
5	0.817E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.919E-10	0.503E-09
6	0.208E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.831E-10	0.105E-09
7	0.146E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.800E-10	0.937E-10
LAYER 5 FOR MONTH 13								
1	0.100E+01	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.744E-10	0.366E-06
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.891E-10	0.685E-06
2	0.999E+00	+	KFEODM	0.127E+01	0.398E+02	0.127E+04	0.237E-11	0.237E-08
3	0.209E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.586E-10	0.741E-10
4	0.175E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.635E-10	0.770E-10
5	0.174E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.687E-10	0.831E-10
6	0.147E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.651E-10	0.763E-10
7	0.107E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.676E-10	0.756E-10
LAYER 11 FOR MONTH 13								
1	0.100E+01	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.558E-10	0.130E-05
2	0.999E+00	+	KFEODM	0.127E+01	0.398E+02	0.127E+04	0.178E-11	0.178E-08
3	0.349E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.432E-10	0.663E-10
4	0.278E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.425E-10	0.588E-10
5	0.147E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.488E-10	0.572E-10
LAYER 1 FOR MONTH 18								
1	0.100E+01	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.850E-10	0.285E-06
1	0.100E+01	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.835E-10	0.168E-06
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.903E-10	0.432E-01
2	0.999E+00	+	KFEODM	0.127E+01	0.398E+02	0.127E+04	0.837E-08	0.837E-05
3	0.953E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.109E-06	0.232E-05
4	0.931E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.726E-07	0.105E-05
5	0.715E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.141E-06	0.496E-06
6	0.559E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.169E-06	0.383E-06
7	0.362E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.172E-06	0.270E-06
8	0.177E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.243E-06	0.295E-06
9	0.127E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.244E-06	0.280E-06
LAYER 5 FOR MONTH 18								
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.906E-10	0.379E-06
2	0.999E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.788E-10	0.158E-06
2	0.999E+00	+	KFEODM	0.127E+01	0.398E+02	0.127E+04	0.251E-11	0.251E-08
3	0.248E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.589E-10	0.784E-10
4	0.184E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.723E-10	0.886E-10
5	0.161E+00	+	V3	0.100E-02	0.500E-02	0.100E-01	0.679E-10	0.809E-10
6	0.137E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.695E-10	0.805E-10
7	0.113E+00	+	V2	0.100E-02	0.500E-02	0.100E-01	0.711E-10	0.801E-10

SENSITIVITY OF INPUTS ON FE3T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
8	0.111E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.791E-10	0.889E-10

LAYER 11 FOR MONTH 18

1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.587E-10	0.208E-05
2	0.999E+00	+	KFED0H	0.127E+01	0.398E+02	0.127E+04	0.187E-11	0.187E-08
3	0.384E+00	+	SATCT	0.100E-02	0.350E-02	0.100E-01	0.439E-10	0.712E-10
4	0.297E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.419E-10	0.596E-10

LAYER 1 FOR MONTH 121

1	0.100E+01	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.607E-06	0.184E-02
1	0.100E+01	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.579E-08	0.184E-02
2	0.998E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.607E-06	0.263E-03
2	0.998E+00	+	KFED0H	0.127E+01	0.398E+02	0.127E+04	0.845E-05	0.397E-02
3	0.997E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.815E-06	0.263E-03
3	0.997E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.815E-06	0.263E-03
3	0.997E+00	+	F1	0.670E+00	0.840E+00	0.101E+01	0.709E-06	0.228E-03
3	0.997E+00	-	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.628E-06	0.248E-03
4	0.996E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.816E-06	0.189E-03
4	0.996E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.816E-06	0.189E-03
5	0.992E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.150E-05	0.189E-03
5	0.992E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.110E-05	0.136E-03
6	0.986E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.716E-05	0.507E-03
7	0.948E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.104E-09	0.202E-08
8	0.910E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.981E-05	0.109E-03
9	0.900E+00	+	V12	0.100E-02	0.500E-02	0.100E-01	0.190E-04	0.189E-03
10	0.897E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.189E-03	0.184E-02
11	0.312E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.186E-03	0.270E-03
12	0.280E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.189E-03	0.263E-03
12	0.280E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.189E-03	0.263E-03
12	0.280E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.189E-03	0.263E-03
12	0.280E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.189E-03	0.263E-03
12	0.280E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.189E-03	0.263E-03
13	0.266E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.104E-09	0.142E-09

LAYER 5 FOR MONTH 121

1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.830E-07	0.282E-01
1	0.100E+01	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.105E-06	0.138E-01
2	0.932E+00	+	KFED0H	0.127E+01	0.398E+02	0.127E+04	0.208E-02	0.307E-01
3	0.909E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.298E-02	0.329E-01
4	0.856E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.215E-02	0.149E-01
5	0.791E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.927E-02	0.443E-01
6	0.735E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.401E-02	0.151E-01
7	0.539E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.106E-01	0.230E-01
8	0.522E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.106E-01	0.222E-01
9	0.407E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.921E-02	0.155E-01
10	0.380E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.107E-01	0.173E-01
11	0.374E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.958E-02	0.153E-01
12	0.326E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.106E-01	0.158E-01
13	0.269E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.104E-01	0.143E-01
14	0.248E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.107E-01	0.142E-01

SENSITIVITY OF INPUTS ON FE3T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
15	0.247E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.107E-01	0.142E-01
16	0.234E+00	+	V5	0.140E-01	0.700E-01	0.140E+00	0.107E-01	0.139E-01
17	0.228E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.107E-01	0.138E-01
18	0.224E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.107E-01	0.138E-01
19	0.193E+00	-	KCAS04	0.214E-04	0.243E-04	0.273E-04	0.109E-01	0.135E-01
20	0.120E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.116E-01	0.132E-01

LAYER 11 FOR MONTH 121

1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.437E-10	0.374E-01
1	0.100E+01	+	KCONST	0.118E+04	0.230E+07	0.472E+08	0.425E-10	0.880E-01
1	0.100E+01	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.441E-10	0.374E-01
2	0.999E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.112E-07	0.150E-04
3	0.997E+00	-	ME1	-0.500E-01	-0.500E+00	-0.150E+01	0.544E-10	0.180E-07
4	0.684E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.127E-06	0.401E-06
5	0.659E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.211E-06	0.619E-06
6	0.630E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.215E-06	0.581E-06
7	0.584E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.193E-06	0.465E-06
8	0.563E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.231E-06	0.529E-06
9	0.459E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.241E-06	0.446E-06
10	0.458E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.219E-06	0.405E-06
11	0.448E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.218E-06	0.395E-06
12	0.435E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.218E-06	0.387E-06
13	0.429E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.221E-06	0.387E-06
14	0.427E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.222E-06	0.387E-06
15	0.413E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.227E-06	0.386E-06
16	0.403E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.191E-06	0.319E-06
17	0.402E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.230E-06	0.385E-06
18	0.347E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.217E-06	0.332E-06
19	0.343E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.155E-06	0.236E-06
20	0.330E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.214E-06	0.319E-06
21	0.307E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.217E-06	0.313E-06
22	0.305E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.216E-06	0.311E-06
23	0.261E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.186E-06	0.252E-06
24	0.154E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.204E-06	0.241E-06

LAYER 1 FOR MONTH 126

1	0.100E+01	-	KCONST	0.118E+04	0.230E+07	0.472E+08	0.104E-09	0.283E-02
2	0.997E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.104E-09	0.405E-07
3	0.983E+00	+	KFEDOM	0.127E+01	0.398E+02	0.127E+04	0.165E-03	0.991E-02
4	0.945E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.128E-02	0.233E-01
5	0.535E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.130E-02	0.279E-02
6	0.344E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.184E-02	0.280E-02
7	0.320E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.189E-02	0.278E-02
7	0.320E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.185E-02	0.273E-02
8	0.316E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.131E-02	0.192E-02
9	0.306E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.190E-02	0.274E-02
10	0.304E+00	+	ME1	-0.500E-01	-0.500E+00	-0.150E+01	0.193E-02	0.277E-02
11	0.283E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.190E-02	0.265E-02
12	0.278E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.190E-02	0.263E-02
13	0.269E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.192E-02	0.263E-02

SENSITIVITY OF INPUTS ON FET3

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 126								
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.105E-06	0.156E-01
1	0.100E+01	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.477E-07	0.398E-02
2	0.999E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.275E-05	0.233E-02
3	0.989E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.116E-03	0.105E-01
4	0.940E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.893E-03	0.149E-01
5	0.878E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.192E-02	0.157E-01
6	0.696E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.127E-02	0.417E-02
7	0.575E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.277E-02	0.652E-02
8	0.548E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.193E-02	0.427E-02
9	0.536E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.196E-02	0.424E-02
10	0.527E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.283E-02	0.598E-02
11	0.341E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.397E-02	0.602E-02
12	0.298E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.288E-02	0.410E-02
13	0.286E+00	-	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.291E-02	0.408E-02

LAYER 11 FOR MONTH 126								
1	0.100E+01	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.304E-06	0.450E-01
1	0.100E+01	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.111E-05	0.975E-01
1	0.100E+01	+	FALOH	0.100E-01	0.750E-01	0.600E+00	0.559E-10	0.458E-01
1	0.100E+01	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.581E-08	0.182E-04
2	0.999E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.490E-10	0.578E-07
3	0.702E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.278E-06	0.932E-06
4	0.656E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.109E-06	0.317E-06
5	0.496E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.261E-06	0.518E-06
6	0.482E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.264E-06	0.510E-06
7	0.481E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.266E-06	0.512E-06
8	0.442E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.266E-06	0.478E-06
9	0.403E+00	-	KBAS	0.217E+02	0.227E+02	0.237E+02	0.310E-06	0.519E-06
10	0.385E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.277E-06	0.450E-06
11	0.301E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.275E-06	0.393E-06
12	0.297E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.230E-06	0.327E-06
13	0.260E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.240E-06	0.324E-06
14	0.125E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.275E-06	0.315E-06
15	0.116E+00	+	F2	0.399E+00	0.499E+00	0.599E+00	0.263E-06	0.297E-06
16	0.104E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.277E-06	0.309E-06

Table F.5.12
Sensitivity Analysis
on Porewater pH

SENSITIVITY OF INPUTS ON PH

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.681E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.200E+01	0.626E+01
2	0.356E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.405E+01	0.629E+01
2	0.356E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.405E+01	0.629E+01
3	0.340E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.415E+01	0.629E+01
4	0.150E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.535E+01	0.629E+01
LAYER 5 FOR MONTH 13								
1	0.451E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.355E+01	0.647E+01
2	0.446E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.350E+01	0.631E+01
LAYER 11 FOR MONTH 13								
1	0.485E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.350E+01	0.680E+01
2	0.119E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.658E+01	0.748E+01
3	0.113E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.673E+01	0.758E+01
LAYER 1 FOR MONTH 18								
1	0.730E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.170E+01	0.630E+01
2	0.441E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.355E+01	0.635E+01
3	0.435E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.360E+01	0.637E+01
LAYER 5 FOR MONTH 18								
1	0.439E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.360E+01	0.642E+01
2	0.437E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.355E+01	0.630E+01
LAYER 11 FOR MONTH 18								
1	0.487E+00	+	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.345E+01	0.673E+01
2	0.128E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.671E+01	0.769E+01
3	0.119E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.651E+01	0.739E+01
LAYER 1 FOR MONTH 121								
1	0.540E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.200E+01	0.435E+01
2	0.385E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.200E+01	0.325E+01
3	0.292E+00	+	XALDH3	0.140E-02	0.230E-02	0.320E-02	0.230E+01	0.325E+01
3	0.292E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.230E+01	0.325E+01
4	0.292E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.230E+01	0.325E+01
5	0.281E+00	+	V9	0.100E-01	0.500E-01	0.100E+00	0.230E+01	0.320E+01
5	0.281E+00	+	V11	0.800E-02	0.400E-01	0.800E-01	0.230E+01	0.320E+01
6	0.266E+00	-	UNAX	0.115E+02	0.130E+02	0.145E+02	0.235E+01	0.320E+01
6	0.266E+00	+	NT1	0.450E+00	0.500E+00	0.550E+00	0.235E+01	0.320E+01
7	0.242E+00	+	EA1	0.100E+05	0.117E+05	0.256E+05	0.235E+01	0.310E+01
8	0.238E+00	-	NR1	0.500E-01	0.800E-01	0.110E+00	0.240E+01	0.315E+01
9	0.234E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.475E+01	0.620E+01
10	0.228E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.220E+01	0.285E+01
11	0.149E+00	+	FALDH	0.100E-01	0.750E-01	0.600E+00	0.200E+01	0.235E+01
12	0.130E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.235E+01	0.270E+01
13	0.125E+00	+	V1	0.100E-02	0.500E-02	0.100E-01	0.245E+01	0.280E+01



SENSITIVITY OF INPUTS ON PH

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 5 FOR MONTH 121								
1	0.527E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.175E+01	0.370E+01
2	0.514E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.180E+01	0.370E+01
3	0.311E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.155E+01	0.225E+01
4	0.125E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.175E+01	0.200E+01
5	0.122E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.180E+01	0.205E+01
LAYER 11 FOR MONTH 121								
1	0.776E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.170E+01	0.758E+01
2	0.764E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.175E+01	0.742E+01
3	0.763E+00	-	FALDH	0.100E-01	0.750E-01	0.600E+00	0.175E+01	0.737E+01
4	0.415E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.400E+01	0.684E+01
LAYER 1 FOR MONTH 126								
1	0.677E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.200E+01	0.620E+01
2	0.387E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.380E+01	0.620E+01
3	0.191E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.190E+01	0.235E+01
4	0.167E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.175E+01	0.210E+01
LAYER 5 FOR MONTH 126								
1	0.507E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.180E+01	0.365E+01
2	0.487E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.195E+01	0.380E+01
3	0.317E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.205E+01	0.300E+01
4	0.170E+00	+	KFEODH	0.127E+01	0.398E+02	0.127E+04	0.195E+01	0.235E+01
5	0.163E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.180E+01	0.215E+01
6	0.122E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.180E+01	0.205E+01
LAYER 11 FOR MONTH 126								
1	0.750E+00	-	FALDH	0.100E-01	0.750E-01	0.600E+00	0.170E+01	0.680E+01
2	0.529E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.165E+01	0.350E+01
3	0.521E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.170E+01	0.355E+01
4	0.467E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.375E+01	0.704E+01

Table F.5.13
Sensitivity Analysis
SO₄²⁺ Concentration

SENSITIVITY OF INPUTS ON SO₄

	RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13									
1	0.443E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.105E-01	0.189E-01	
2	0.323E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.997E-02	0.147E-01	
3	0.298E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.967E-02	0.138E-01	
4	0.103E+00	+	KCASO4	0.214E-04	0.245E-04	0.275E-04	0.107E-01	0.119E-01	
LAYER 5 FOR MONTH 13									
1	0.855E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.123E-01	0.849E-01	
2	0.594E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.215E-01	0.530E-01	
3	0.583E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.248E-01	0.595E-01	
4	0.519E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.224E-01	0.464E-01	
5	0.400E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.232E-01	0.386E-01	
6	0.269E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.239E-01	0.327E-01	
7	0.213E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.241E-01	0.307E-01	
8	0.113E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.237E-01	0.267E-01	
LAYER 11 FOR MONTH 13									
1	0.935E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.166E-01	0.255E+00	
2	0.702E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.520E-01	0.174E+00	
3	0.620E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.266E-01	0.701E-01	
4	0.475E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.473E-01	0.900E-01	
5	0.442E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.476E-01	0.853E-01	
6	0.441E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.479E-01	0.857E-01	
7	0.348E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.504E-01	0.773E-01	
8	0.335E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.493E-01	0.741E-01	
9	0.295E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.429E-01	0.609E-01	
10	0.231E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.504E-01	0.655E-01	
11	0.209E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.496E-01	0.627E-01	
12	0.198E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.506E-01	0.632E-01	
13	0.196E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.507E-01	0.630E-01	
14	0.134E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.511E-01	0.590E-01	
LAYER 1 FOR MONTH 18									
1	0.843E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.241E-01	0.153E+00	
2	0.808E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.181E-01	0.939E-01	
3	0.688E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.134E-01	0.427E-01	
4	0.537E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.107E-01	0.232E-01	
5	0.536E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.143E-01	0.309E-01	
6	0.246E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.313E-01	0.415E-01	
7	0.237E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.342E-01	0.449E-01	
8	0.194E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.348E-01	0.432E-01	
9	0.188E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.323E-01	0.398E-01	
10	0.174E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.345E-01	0.418E-01	
11	0.131E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.357E-01	0.411E-01	
LAYER 5 FOR MONTH 18									
1	0.824E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.109E-01	0.620E-01	
2	0.532E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.166E-01	0.355E-01	
3	0.469E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.169E-01	0.319E-01	



SENSITIVITY OF INPUTS ON S04

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
4	0.399E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.173E-01	0.287E-01
5	0.360E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.117E-01	0.182E-01
6	0.339E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.185E-01	0.280E-01
7	0.220E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.129E-01	0.165E-01
8	0.193E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.180E-01	0.223E-01
9	0.171E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.171E-01	0.206E-01
10	0.102E+00	+	SATCT	0.100E-02	0.550E-02	0.100E-01	0.164E-01	0.183E-01
11	0.100E+00	-	V4	0.180E-01	0.900E-01	0.180E+00	0.182E-01	0.203E-01

LAYER 11 FOR MONTH 18

1	0.968E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.179E-01	0.565E+00
2	0.745E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.504E-01	0.198E+00
3	0.484E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.276E-01	0.535E-01
4	0.457E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.461E-01	0.848E-01
5	0.452E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.481E-01	0.878E-01
6	0.406E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.469E-01	0.788E-01
7	0.404E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.469E-01	0.786E-01
8	0.389E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.471E-01	0.770E-01
9	0.294E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.417E-01	0.590E-01
10	0.254E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.486E-01	0.652E-01
11	0.233E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.476E-01	0.621E-01
12	0.172E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.493E-01	0.595E-01
13	0.139E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.495E-01	0.575E-01

LAYER 1 FOR MONTH 121

1	0.345E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.754E-02	0.115E-01
2	0.212E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.795E-02	0.101E-01
3	0.208E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.797E-02	0.101E-01
4	0.204E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.848E-02	0.106E-01
5	0.133E+00	+	FALON	0.100E-01	0.750E-01	0.600E+00	0.795E-02	0.918E-02
6	0.122E+00	-	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.803E-02	0.915E-02
7	0.101E+00	-	IPYR	0.480E-01	0.600E-01	0.720E-01	0.880E-02	0.979E-02

LAYER 5 FOR MONTH 121

1	0.581E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.152E-01	0.363E-01
2	0.470E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.135E-01	0.256E-01
3	0.405E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.135E-01	0.227E-01
4	0.387E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.146E-01	0.238E-01
5	0.236E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.127E-01	0.167E-01
6	0.162E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.153E-01	0.182E-01
7	0.158E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.139E-01	0.165E-01
8	0.155E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.145E-01	0.171E-01
9	0.144E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.148E-01	0.173E-01
10	0.115E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.169E-01	0.191E-01
11	0.106E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.151E-01	0.169E-01
11	0.106E+00	+	V7	0.400E-02	0.200E-01	0.400E-01	0.151E-01	0.169E-01
12	0.101E+00	+	V6	0.600E-02	0.300E-01	0.600E-01	0.152E-01	0.169E-01

LAYER 11 FOR MONTH 121

1	0.858E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.480E-01	0.338E+00
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SENSITIVITY OF INPUTS ON S04

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
2	0.840E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.291E-01	0.182E+00
3	0.826E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.292E-01	0.168E+00
4	0.777E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.384E-01	0.119E+00
5	0.651E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.122E-01	0.348E-01
6	0.610E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.436E-01	0.112E+00
7	0.570E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.447E-01	0.104E+00
8	0.544E+00	-	NT1	0.450E+00	0.500E+00	0.550E+00	0.460E-01	0.101E+00
9	0.534E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.457E-01	0.980E-01
10	0.521E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.457E-01	0.955E-01
11	0.515E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.424E-01	0.875E-01
12	0.514E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.464E-01	0.954E-01
13	0.511E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.467E-01	0.954E-01
14	0.495E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.481E-01	0.952E-01
15	0.482E+00	+	IALOH3	0.140E-02	0.230E-02	0.320E-02	0.493E-01	0.950E-01
16	0.347E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.363E-01	0.556E-01
17	0.245E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.376E-01	0.498E-01
18	0.207E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.494E-01	0.623E-01
19	0.147E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.435E-01	0.509E-01
20	0.136E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.453E-01	0.524E-01
21	0.129E+00	+	UNAX	0.115E+02	0.130E+02	0.145E+02	0.434E-01	0.498E-01
22	0.107E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.444E-01	0.498E-01

LAYER 1 FOR MONTH 126

1	0.357E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.115E-01	0.179E-01
2	0.306E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.102E-01	0.147E-01
3	0.245E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.987E-02	0.131E-01
4	0.226E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.987E-02	0.128E-01
5	0.196E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.120E-01	0.149E-01

LAYER 5 FOR MONTH 126

1	0.404E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.127E-01	0.212E-01
2	0.346E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.985E-02	0.151E-01
3	0.311E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.113E-01	0.164E-01
4	0.292E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.123E-01	0.173E-01
5	0.290E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.109E-01	0.153E-01
6	0.251E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.119E-01	0.159E-01
7	0.237E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.172E-01	0.225E-01
8	0.147E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.125E-01	0.147E-01
9	0.142E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.114E-01	0.133E-01

LAYER 11 FOR MONTH 126

1	0.750E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.366E-01	0.146E+00
1	0.750E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.190E-01	0.762E-01
2	0.730E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.246E-01	0.913E-01
3	0.508E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.243E-01	0.494E-01
4	0.495E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.413E-01	0.818E-01
5	0.486E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.351E-01	0.682E-01
6	0.482E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.242E-01	0.467E-01
7	0.411E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.416E-01	0.706E-01
8	0.386E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.315E-01	0.514E-01

SENSITIVITY OF INPUTS ON SD4

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
9	0.377E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.379E-01	0.608E-01
10	0.353E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.385E-01	0.596E-01
11	0.351E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.389E-01	0.600E-01
12	0.339E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.336E-01	0.509E-01
13	0.291E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.390E-01	0.550E-01
14	0.195E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.411E-01	0.511E-01
15	0.163E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.408E-01	0.489E-01
16	0.158E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.386E-01	0.458E-01
17	0.138E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.411E-01	0.477E-01
18	0.126E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.392E-01	0.449E-01

Table F.5.14
Sensitivity Analysis
on Total Sulphate Concentration

SENSITIVITY OF INPUTS ON SO4T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
LAYER 1 FOR MONTH 13								
1	0.452E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.177E-01	0.324E-01
2	0.314E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.183E-01	0.267E-01
3	0.191E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.174E-01	0.215E-01
4	0.153E+00	+	KCASD4	0.214E-04	0.245E-04	0.275E-04	0.174E-01	0.206E-01
LAYER 5 FOR MONTH 13								
1	0.894E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.200E-01	0.189E+00
2	0.735E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.326E-01	0.123E+00
3	0.518E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.293E-01	0.607E-01
4	0.444E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.301E-01	0.542E-01
5	0.333E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.309E-01	0.464E-01
6	0.218E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.316E-01	0.404E-01
7	0.170E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.319E-01	0.384E-01
LAYER 11 FOR MONTH 13								
1	0.907E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.244E-01	0.262E+00
2	0.828E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.597E-01	0.348E+00
3	0.559E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.344E-01	0.779E-01
4	0.437E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.550E-01	0.978E-01
5	0.405E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.554E-01	0.930E-01
6	0.404E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.557E-01	0.935E-01
7	0.316E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.582E-01	0.850E-01
8	0.303E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.570E-01	0.818E-01
9	0.262E+00	+	IPYR	0.480E-01	0.600E-01	0.720E-01	0.507E-01	0.686E-01
10	0.207E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.581E-01	0.733E-01
11	0.186E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.573E-01	0.704E-01
12	0.177E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.584E-01	0.709E-01
13	0.175E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.584E-01	0.708E-01
14	0.118E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.589E-01	0.668E-01
LAYER 1 FOR MONTH 18								
1	0.888E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.478E-01	0.425E+00
2	0.832E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.355E-01	0.240E+00
3	0.792E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.185E-01	0.889E-01
4	0.775E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.211E-01	0.937E-01
5	0.656E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.221E-01	0.642E-01
6	0.384E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.648E-01	0.105E+00
7	0.249E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.664E-01	0.885E-01
8	0.194E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.785E-01	0.974E-01
9	0.141E+00	+	UMAX	0.115E+02	0.130E+02	0.145E+02	0.791E-01	0.920E-01
10	0.106E+00	-	WT1	0.450E+00	0.500E+00	0.550E+00	0.813E-01	0.908E-01
LAYER 5 FOR MONTH 18								
1	0.853E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.187E-01	0.127E+00
2	0.558E+00	-	XCACD3	0.000E+00	0.500E-03	0.100E-02	0.262E-01	0.594E-01
3	0.437E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.244E-01	0.433E-01
4	0.377E+00	-	V6	0.600E-02	0.300E-01	0.600E-01	0.247E-01	0.396E-01
5	0.314E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.250E-01	0.365E-01

SENSITIVITY OF INPUTS ON S04T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
6	0.253E+00	-	XP	0.320E-03	0.160E-02	0.780E-02	0.194E-01	0.260E-01
7	0.150E+00	-	XPYR	0.480E-01	0.600E-01	0.720E-01	0.206E-01	0.243E-01
8	0.144E+00	-	V5	0.140E-01	0.700E-01	0.140E+00	0.257E-01	0.301E-01
9	0.124E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.248E-01	0.284E-01
10	0.107E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.247E-01	0.276E-01

LAYER 11 FOR MONTH 18

1	0.955E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.256E-01	0.573E+00
2	0.870E+00	-	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.581E-01	0.447E+00
3	0.423E+00	-	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.353E-01	0.612E-01
4	0.418E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.539E-01	0.926E-01
5	0.415E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.558E-01	0.955E-01
6	0.369E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.546E-01	0.866E-01
7	0.367E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.546E-01	0.864E-01
8	0.333E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.540E-01	0.848E-01
9	0.260E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.494E-01	0.668E-01
10	0.227E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.563E-01	0.729E-01
11	0.207E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.554E-01	0.698E-01
12	0.152E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.570E-01	0.673E-01
13	0.123E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.573E-01	0.653E-01

LAYER 1 FOR MONTH 121

1	0.199E+00	-	F2	0.399E+00	0.499E+00	0.599E+00	0.174E-01	0.217E-01
2	0.150E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.179E-01	0.210E-01
3	0.141E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.181E-01	0.211E-01
4	0.110E+00	+	KCAS04	0.214E-04	0.245E-04	0.275E-04	0.175E-01	0.196E-01
5	0.109E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.182E-01	0.204E-01

LAYER 5 FOR MONTH 121

1	0.613E+00	+	XP	0.320E-03	0.160E-02	0.780E-02	0.322E-01	0.831E-01
2	0.560E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.402E-01	0.913E-01
3	0.405E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.294E-01	0.495E-01
4	0.389E+00	+	KCONST	0.118E+06	0.230E+07	0.472E+08	0.441E-01	0.721E-01
5	0.383E+00	-	EA1	0.100E+05	0.117E+05	0.256E+05	0.308E-01	0.500E-01
6	0.364E+00	+	KBAS	0.217E+02	0.227E+02	0.237E+02	0.463E-01	0.720E-01
7	0.334E+00	+	KFEDDH	0.127E+01	0.398E+02	0.127E+04	0.411E-01	0.618E-01
8	0.247E+00	-	V9	0.100E-01	0.500E-01	0.100E+00	0.450E-01	0.597E-01
9	0.222E+00	-	V10	0.100E-01	0.500E-01	0.100E+00	0.450E-01	0.579E-01
10	0.219E+00	+	NR1	0.500E-01	0.800E-01	0.110E+00	0.399E-01	0.512E-01
11	0.193E+00	-	V11	0.800E-02	0.400E-01	0.800E-01	0.455E-01	0.563E-01
12	0.182E+00	+	XPYR	0.480E-01	0.600E-01	0.720E-01	0.413E-01	0.505E-01
13	0.133E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.451E-01	0.520E-01

LAYER 11 FOR MONTH 121

1	0.613E+00	-	V12	0.100E-02	0.500E-02	0.100E-01	0.762E-01	0.197E+00
2	0.596E+00	-	V7	0.400E-02	0.200E-01	0.400E-01	0.844E-01	0.209E+00
3	0.561E+00	-	V8	0.600E-02	0.300E-01	0.400E-01	0.862E-01	0.196E+00
4	0.505E+00	+	XCAC03	0.000E+00	0.500E-03	0.100E-02	0.937E-01	0.189E+00
5	0.501E+00	+	HE1	-0.500E-01	-0.500E+00	-0.150E+01	0.212E-01	0.426E-01
6	0.491E+00	-	KCONST	0.118E+06	0.230E+07	0.472E+08	0.176E+00	0.346E+00

SENSITIVITY OF INPUTS ON S04T

RANK	SENSITIVITY	SIGN	INPUT	MINIMUM	MODE	MAXIMUM	MINIMUM OUTPUT	MAXIMUM OUTPUT
7	0.484E+00	-	WT1	0.450E+00	0.500E+00	0.550E+00	0.882E-01	0.171E+00
8	0.480E+00	-	F1	0.670E+00	0.840E+00	0.101E+01	0.859E-01	0.165E+00
9	0.474E+00	-	V3	0.100E-02	0.500E-02	0.100E-01	0.878E-01	0.167E+00
10	0.467E+00	-	FALOH	0.100E-01	0.750E-01	0.600E+00	0.938E-01	0.176E+00
11	0.462E+00	-	V2	0.100E-02	0.500E-02	0.100E-01	0.878E-01	0.163E+00
12	0.455E+00	-	SATCT	0.100E-02	0.550E-02	0.100E-01	0.889E-01	0.163E+00
13	0.452E+00	-	V1	0.100E-02	0.500E-02	0.100E-01	0.893E-01	0.163E+00
14	0.438E+00	+	V4	0.180E-01	0.900E-01	0.180E+00	0.916E-01	0.163E+00
15	0.426E+00	+	XALOH3	0.140E-02	0.230E-02	0.320E-02	0.934E-01	0.163E+00



APPENDIX G
REACTION-PATH-CODE CALCULATIONS

C-8206.195.11

CHEMICAL MODELLING OF
PYRITE DISSOLUTION

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1. INTRODUCTION

This report presents the results of a chemical-modelling project done for BEAK CONSULTANTS LIMITED during the period 1986 February to March. The objective of the study was to carry out modelling work in support of source-term development projects, on pyritic uranium mill tailings, carried out by BEAK CONSULTANTS LIMITED for the National Uranium Tailings Program [1]. The present work is an extension of the preliminary studies presented in References 2-4. The major focus of the present report is on the non-equilibrium between pyrite and its environment. The models used in the present report are based on the discussions of pyrite oxidation given in References 5-7.

Section 2 presents a kinetic model of the system.

Section 3 describes reaction path simulations.

Section 4 summarizes the conclusions from the calculations.

2. A KINETIC MODEL

The oxidative dissolution of pyrite can be described by the simple kinetic model shown in Figure 1 [5,6]. The rate laws for the aqueous oxidation of pyrite by O_2 (reaction 1), the oxidation of ferrous ion (reaction 2) and the oxidation of pyrite by ferric ion (reaction 3) have been reviewed by Lawson [7].

The rate of oxidation of pyrite by molecular oxygen is first order in the partial pressure of oxygen and is independent of solution composition, i.e., the concentration of H^+ , Fe^{2+} or Fe^{3+} ,

$$-\frac{d[FeS_2]}{dt} = k_1' p(O_2) = k_1 ; \quad \text{Rate Law for Reaction 1.}$$

The reaction order for the oxidation of ferrous iron by molecular oxygen is a function of the media, pH, ferrous ion concentration, etc. [7]. In the pH range 2 to 5, the rate law for reaction 2 is given by

$$-\frac{d[Fe^{2+}]}{dt} = k_2' p(O_2) [OH^-] [Fe^{2+}] = k_2 [Fe^{2+}] ; \quad \text{Rate Law for Reaction 2.}$$

The rate law for the oxidation of pyrite by ferric ion is not well known [7]. The rate depends on pH and on the fraction of pyrite surface occupied by ferric ion, i.e., on the ratio $[Fe^{3+}]/([Fe^{2+}] + [Fe^{3+}])$. We select the following rate law for the oxidation of pyrite by ferric ion [7],

$$-\frac{d[Fe^{3+}]}{dt} = \frac{k_3' [Fe^{3+}] [OH^-]^{0.44}}{[Fe^{2+}] + [Fe^{3+}]} = k_3 [Fe^{3+}] ; \quad \text{Rate Law for Reaction 3.}$$

Finally, for the formation of amorphous ferric hydroxide we choose the rate law

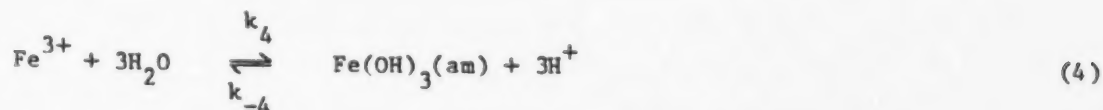
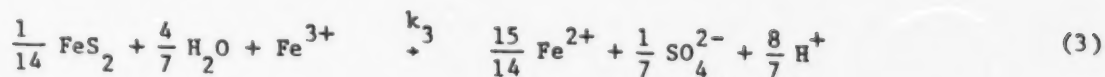
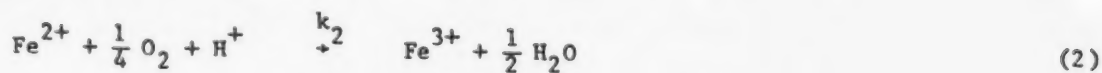
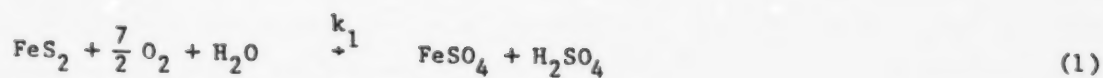
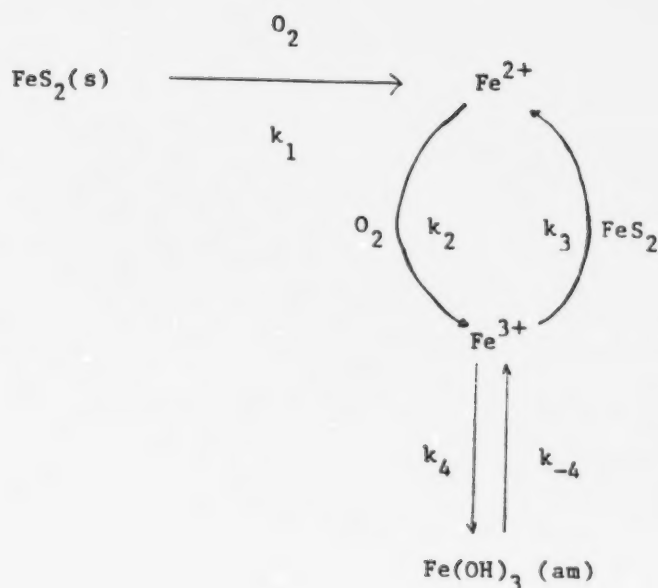


Figure 1. Kinetic Model for Pyrite Dissolution

$$-\frac{d[Fe^{3+}]}{dt} = k_4[Fe^{3+}] - k_{-4} ; \quad \text{Rate Law for Reaction 4.}$$

With these rate laws we can describe the oxidative dissolution of pyrite by using the kinetic equations

$$\frac{d[FeS_2]}{dt} = -k_1 - k_3[Fe^{3+}]/14 \quad (5a)$$

$$\frac{d[Fe^{2+}]}{dt} = k_1 - k_2[Fe^{2+}] + 15k_3[Fe^{3+}]/14 \quad (5b)$$

$$\frac{d[Fe^{3+}]}{dt} = k_2[Fe^{2+}] - (k_3+k_4)[Fe^{3+}] + k_{-4} \quad (5c)$$

$$\frac{d[Fe(OH)_3(am)]}{dt} = k_4[Fe^{3+}] - k_{-4} \quad (5d)$$

The kinetic equations (5) are very difficult to solve analytically since the rate constants depend on pH and $p(O_2)$. However, in many cases, the pH changes produced by the oxidative dissolution of pyrite will be buffered by the presence of such solids as calcium carbonate or gibbsite. Therefore, as a first approximation, it will be assumed that the pH and the oxygen partial pressure, $p(O_2)$, vary slowly as the pyrite is dissolved. Effects due to changes in the pH over long periods of time can, in this approximation, be accounted for by varying the values of the rate constants, k_1 , after the pH has changed significantly.

The kinetic equations (5) are linear if the rate constants, k_1 , are time independent. Thus, their solution can be obtained analytically:

$$[Fe^{2+}]_t = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) + C \quad (6a)$$

$$[Fe^{3+}]_t = X \exp(-\lambda_1 t) + Y \exp(-\lambda_2 t) + Z \quad (6b)$$

$$[\text{FeS}_2]_t = [\text{FeS}_2]_0 - k_1 t - (k_3/14) \int_0^t [\text{Fe}^{3+}]_t dt \quad (6c)$$

and

$$[\text{Fe}(\text{OH})_3(\text{am})]_t = [\text{Fe}(\text{OH})_3(\text{am})]_0 - k_{-4} t + k_4 \int_0^t [\text{Fe}^{3+}]_t dt \quad (6d)$$

In these equations,

$$\lambda_{1,2} = \frac{1}{2} (k_2 + k_3 + k_4) \pm \frac{1}{2} \sqrt{(k_2 + k_3 + k_4)^2 + \frac{2}{7} k_2 k_3 - 4k_2 k_4},$$

$$Z = (k_1 + k_{-4}) / (k_4 - k_3/14)$$

and

$$C = (k_1 + 15k_3 Z/14)(k_2)^{-1}$$

A, B, X and Y are obtained by solving the equations

$$A + B + C = [\text{Fe}^{2+}]_0$$

$$X + Y + Z = [\text{Fe}^{3+}]_0$$

$$A = (k_3 + k_4 - \lambda_1)X/k_2$$

and

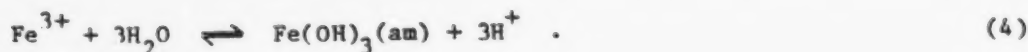
$$B = (k_3 + k_4 - \lambda_2)Y/k_2$$

The subscript 0 denotes the $t = 0$ value of the concentrations.

The solutions (6) to the kinetic equations (5) are difficult to interpret unless explicit calculations are carried out using the appropriate values of the rate constants k_1 . However, under certain approximations, equations (6) can be reduced to a much simpler form.

Let us assume that $\text{Fe}(\text{OH})_3(\text{am})$ is in rapid equilibrium with Fe^{3+} , i.e., the rate constants k_4 and k_{-4} are much larger than k_1 , k_2 and k_3 . In

this case, the concentration $[Fe^{3+}]$ is controlled by the equilibrium



Therefore, as long as $Fe(OH)_3(am)$ is available,

$$[Fe^{3+}]_e = [H^+]^3 / K_4$$

where K_4 is the equilibrium constant for reaction (4). With this value of the concentration $[Fe^{3+}]$, the kinetic equations (5) reduce to the simpler form

$$\frac{d[FeS_2]}{dt} = -k_1 - k_3[Fe^{3+}]_e/14 \quad (7a)$$

$$\frac{d[Fe^{2+}]}{dt} = k_1 - k_2[Fe^{2+}] + 15k_3[Fe^{3+}]_e/14 \quad (7b)$$

$$\frac{d([Fe^{3+}] + [Fe(OH)_3(am)])}{dt} = k_2[Fe^{2+}] - k_3[Fe^{3+}]_e \quad (7c)$$

The solution of equations (7) is given by

$$[FeS_2]_t = [FeS_2]_0 - (k_1 + k_3[Fe^{3+}]_e/14)t \quad (8a)$$

$$[Fe^{2+}]_t = A(1 - \exp(-k_2t)) + [Fe^{2+}]_0 \exp(-k_2t) \quad (8b)$$

$$[Fe(OH)_3(am)]_t = [Fe(OH)_3(am)]_0 + (k_1 + k_3[Fe^{3+}]_e/14)t + ([Fe^{2+}]_0 - A)(1 - \exp(-k_2t)) \quad (8c)$$

where

$$A = (k_1 + 15k_3[Fe^{3+}]_e/14)(k_2)^{-1}.$$

These equations hold for times t such that $[FeS_2]_t \geq 0$. For times $t \gg (k_2)^{-1}$ the concentration $[Fe^{2+}]$ reaches the steady-state value A .

Since the oxidative dissolution of FeS_2 by ferric ion is much faster than

the rate of oxidation of FeS_2 by molecular oxygen ($k_3 \gg k_1$), we find that, at long times,

$$[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 15k_3/14k_2 \quad (9)$$

Because the kinetic model used to describe the oxidative dissolution of pyrite does not incorporate all reactions (e.g., the reverse of reactions 1, 2 and 3 do not appear in the kinetic model), the steady-state value of the ratio $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ given by equation (9) is not equal to the value of $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ calculated from equilibrium calculations. In particular, this value cannot be used to determine the "equilibrium" oxidation potential for the system. Moreover, at equilibrium, one expects

$$[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = [\text{OH}^-]/(\text{p}(\text{O}_2))^{1/4} \quad (10)$$

(see equation (2)), whereas from the rate laws for reactions 2 and 3 one finds that the steady-state value of the ratio $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ given by equation (9) is proportional to $[\text{OH}^-]^{0.44}/\text{p}(\text{O}_2)$, which is quite different from equation (10).

The kinetic model for the oxidative dissolution of pyrite can also be used to determine the change in the hydrogen ion concentration as pyrite dissolves, i.e., $d[\text{H}^+]/dt$. However, in a real system, the changes in pH predicted by the kinetic model would not be accurate since the presence of solids such as $\text{CaCO}_3(\text{s})$, $\text{Al}(\text{OH})_3(\text{s})$ and even $\text{Fe}(\text{OH})_3(\text{am})$ would tend to buffer the pH (see Section 3). Since complete kinetic data are usually not available, it is difficult to incorporate more reactions into the kinetic model. Therefore, the effect of pH buffers must be studied using thermodynamic reaction path calculations.

3. REACTION PATH SIMULATIONS

Reaction path calculations were carried out with the code CHEMP [8]. The special features of this code and examples of its applications to problems involving partial equilibrium conditions are described in References 8 and 9.

A reaction path calculation attempts to simulate solid dissolution processes. When a solid (e.g., pyrite) is initially put in contact with solution (e.g., oxygenated water), the solid-solution system is not in equilibrium and the solid undergoes irreversible dissolution. While this solid is progressively dissolved, a sequence of other solids may precipitate. Some of them may later dissolve. During this process, the system is not in equilibrium with the original solid. The system is then in partial equilibrium [10,11], i.e., all the components of the system, except for the original solid, are in equilibrium. The dissolution process continues until the solution reaches saturation with respect to the original solid. When the original solid starts forming, the system is no longer in "partial equilibrium", but rather in "total equilibrium". In other words, equilibrium is attained between the solution phase, the various solids and the original solid once the original solid (e.g., pyrite) appears in the results of the reaction path calculations.

The conditions for the various cases studied using reaction path calculations for the present project are summarized in Table I. Note that the initial abundances are usually the same as those used in Reference 3. In addition to the solids listed in Table I (amounts given in moles), the systems also contain 1 kg of water and $1.50 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1} \text{ K}^+$.

The thermodynamic database used for the present calculation was discussed in detail in References 2 and 3. A summary of the thermodynamic data is included for completeness in the Appendix.

TABLE I: THE REACTION PATH RUNS

Case Number	pH Mode	Initial pH	FeS ₂ (pyrite)	Fe(OH) ₃ (amorphous)	CaSO ₄ ·2H ₂ O (gypsum)	Al(OH) ₃ (gibbsite)	CaCO ₃ (calcite)	Titratant
R3	float	3	-	1.22	2.22	0.816	0.08	14/13 FeS ₂
R4	float	6	-	1.22	2.22	0.816	0.08	14/13 FeS ₂
R9	fix	3	-	1.22	2.22	0.816	0.08	14/13 FeS ₂
R10	fix	6	-	1.22	2.22	0.816	0.08	14/13 FeS ₂
R1	float	3	-	1.22	2.22	0.816	0.08	14/13 FeS ₂ + 7/2 O ₂ (aq)
R2	float	6	-	1.22	2.22	0.816	0.08	14/13 FeS ₂ + 7/2 O ₂ (aq)
R13	float	3	-	1.22	-	-	-	14/13 FeS ₂ + 7/2 O ₂ (aq)
R7	fix	3	-	1.22	2.22	0.816	0.08	14/13 FeS ₂ + 7/2 O ₂ (aq)
R9	fix	6	-	1.22	2.22	0.816	0.08	14/13 FeS ₂ + 7/2 O ₂ (aq)
R24	float	7	-	1.22	2.22	0.816	0.08	14/13 FeS ₂ + 7/2 O ₂ (aq) 1.35 Fe ²⁺ - 1.25 Fe(OH) ₃ + 2.3 OH ⁻ + 0.2 SO ₄ ²⁻
R27*	float	7	-	1.22	2.22	0.816	0.08	1.35 Fe ²⁺ - 1.25 Fe(OH) ₃ + 2.3 OH ⁻ + 0.2 SO ₄ ²⁻
R29*	fix	3	-	1.22	2.22	0.816	0.08	1.35 Fe ²⁺ - 1.25 Fe(OH) ₃ + 2.3 OH ⁻ + 0.2 SO ₄ ²⁻
R23	float	6	-	1.22	2.22	0.816	0.08	1.35 Fe ²⁺ - 1.25 Fe(OH) ₃ + 2.3 OH ⁻ + 0.2 SO ₄ ²⁻ H ⁺

*No FeS₂, FeS, Fe₇S₈ in database.

3.1 TITRATIONS WITH PYRITE

In this series of reaction path calculations we simulate the process shown schematically in Figure 2:

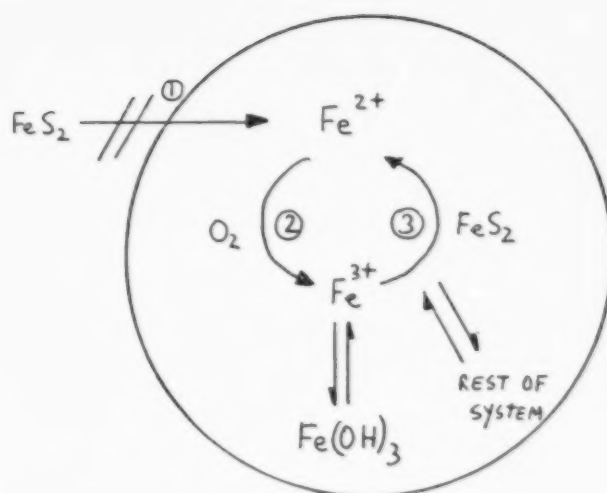


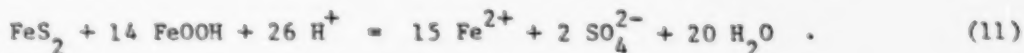
Figure 2. Titrations with Pyrite

The reaction numbers in Figure 2 correspond to the reactions described in Section 2. Here, FeS_2 (pyrite) is not in equilibrium with the rest of the system and partial equilibrium holds until FeS_2 (pyrite) appears in the results. In these simulations we assume that the rate of reaction 1 is much slower than the rates of the other reactions in the system. Only the reactions within the large circle (in Figure 2) are in equilibrium.

3.1.1 Floating pH Calculations

In cases B3 and B4 the system contains the solids: $\text{Fe}(\text{OH})_3$ (amorphous), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), $\text{Al}(\text{OH})_3$ (gibbsite) and CaCO_3 (calcite). The real system would also contain FeS_2 (pyrite); however, the pyrite is not in equilibrium with the rest of the system since its dissolution rate is slow. This is taken into account by introducing pyrite into the simulation as the titrant. In other words, the reaction coordinate, ξ , is proportional to the number of moles of pyrite dissolved per kilogram of solution along the reaction path.

Figures 3-5 describe the changes in H^+ concentration, solid abundances and aqueous species concentrations along the reaction path for case B3. The initial pH values are not maintained and they change from $\text{pH}_1 = 3$ and $\text{pH}_1 = 6$ to $\text{pH} = 7$ and $\text{pH} = 8$ in cases B3 and B4, respectively. The reaction responsible for the increase in pH is:



In these calculations reducing conditions prevail (no oxygen), and therefore pyrite shows up very early along the path. The formation of pyrite signifies a state of total equilibrium and, indeed, none of the abundances (or concentrations) changes as a function of the reaction coordinate once pyrite forms (see Figures 3-5).

3.1.2 Fixed pH Calculations

These cases are similar to cases B3 and B4 except that the pH is fixed at $\text{pH} = 3$ and $\text{pH} = 6$ for cases B9 and B10, respectively. The fixed pH calculations allow us to study the system shown in Figure 2 under lower pH conditions than those imposed by equilibrium constraints. The results for case B9 are shown in Figures 6-8.

It is interesting to note that under acidic pH conditions pyrite does not reach equilibrium until far along the reaction path. For example,

in case B9, pyrite is not in equilibrium with the system until approximately $\xi = 10^{-1}$. The non-equilibrium condition with respect to pyrite occurs in the region $\xi < 10^{-1}$ although the conditions are reducing. This is due to the acidic pH.

The pH conditions also explain the total dissolution of CaCO_3 in case B9.

Note that partial equilibrium prevails in case B9 until the FeOOH dissolves (by reaction with pyrite, equation (11)) and total equilibrium is achieved following FeOOH dissolution and formation of pyrite. From then on, all the abundances and concentrations are constant.

The E_h (3) gradually drops along the reaction path (see Figure 9). This is not surprising and is due to the addition of a reducing agent (i.e., pyrite) along the reaction path.

FIGURE 3

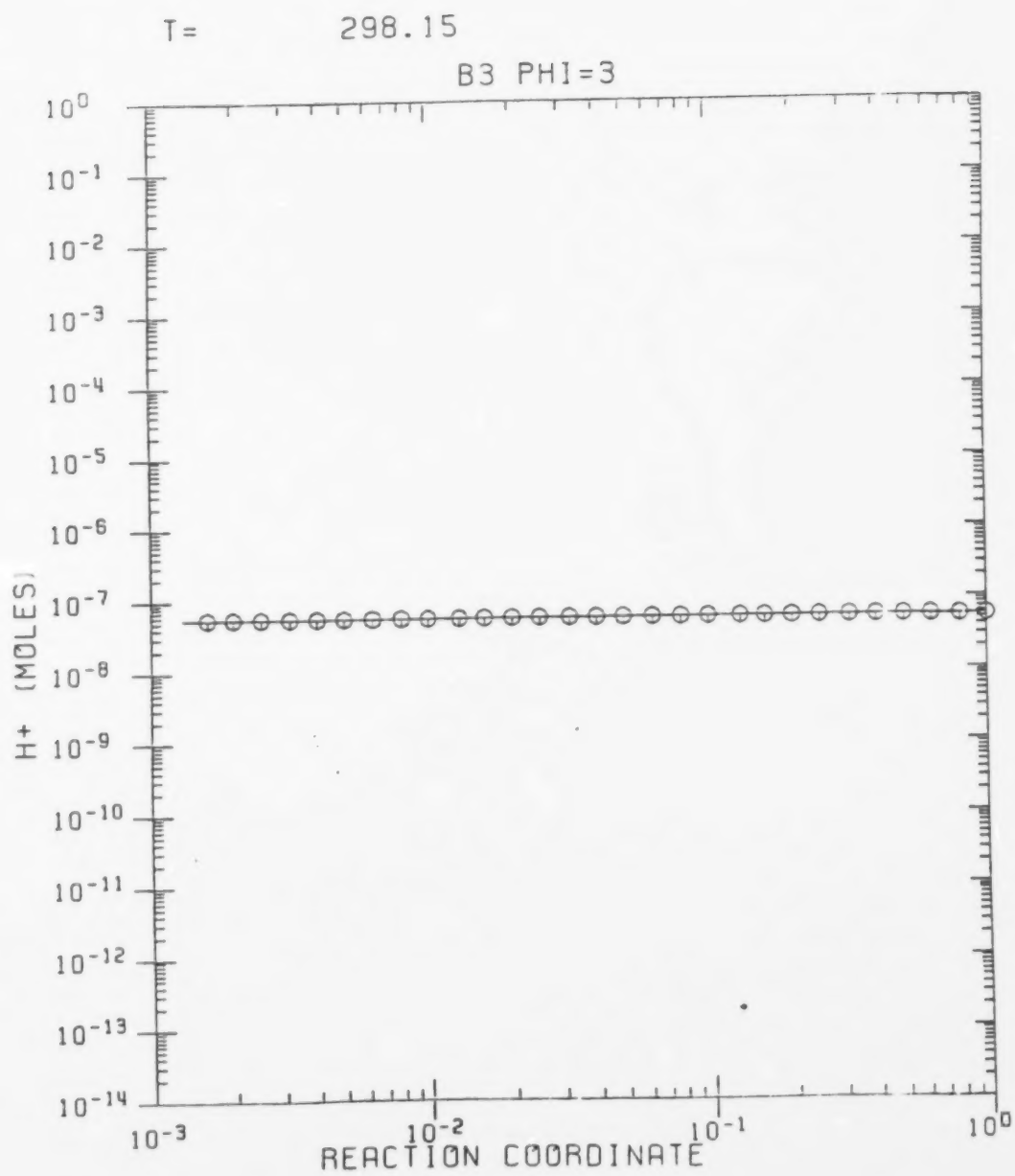


FIGURE 4

T= 298.15

B3 PHI=3

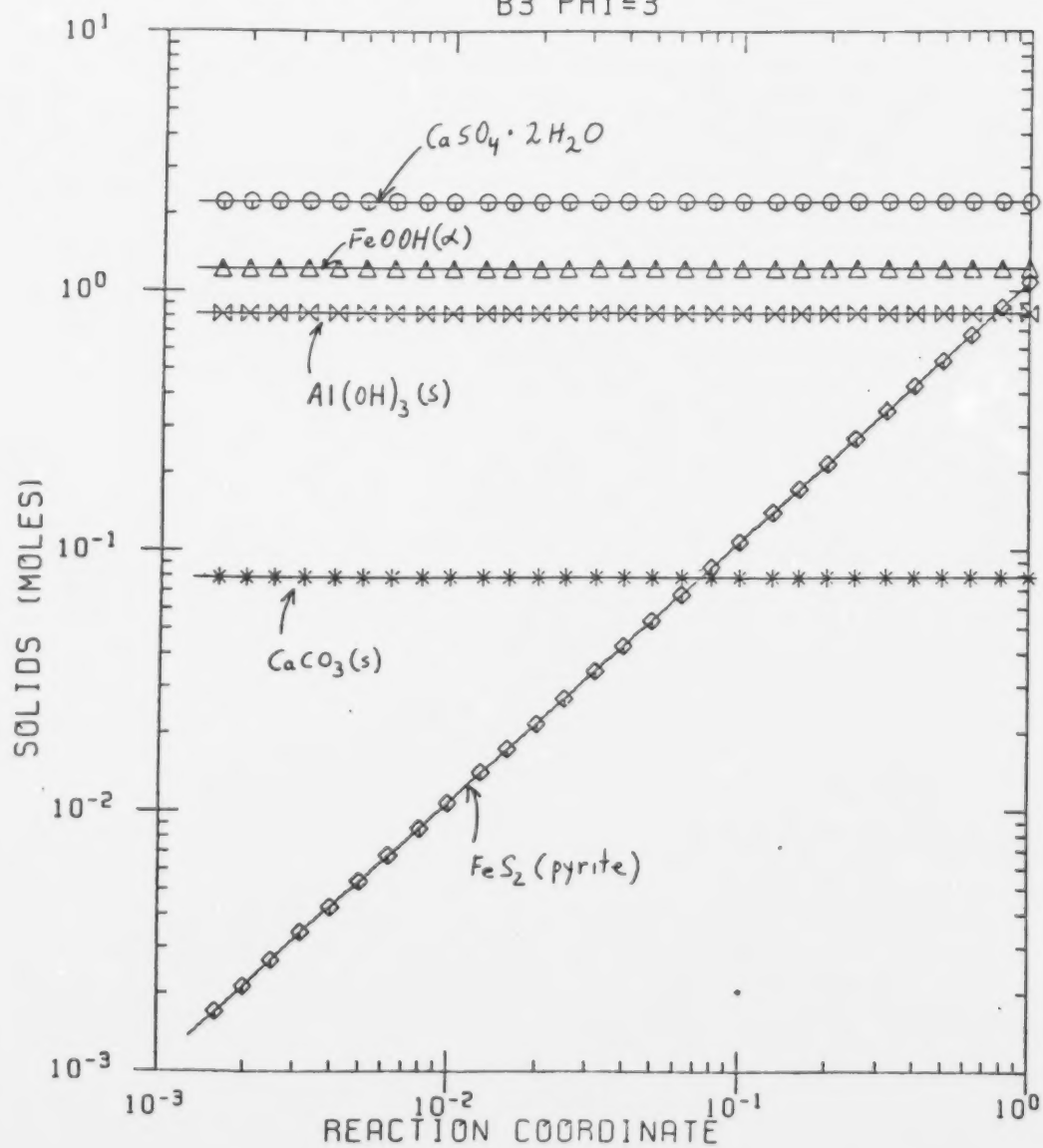


FIGURE 5

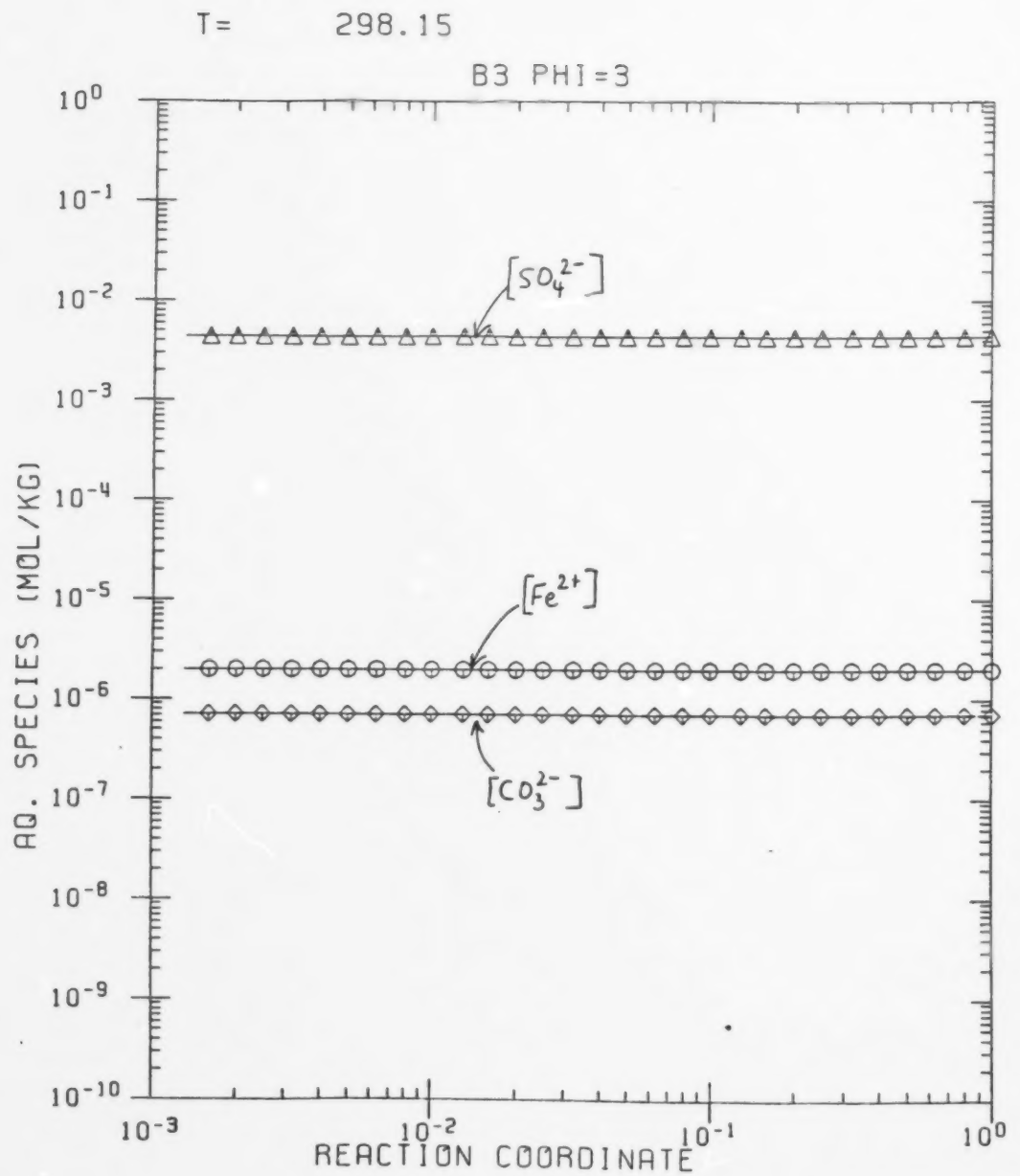


FIGURE 6

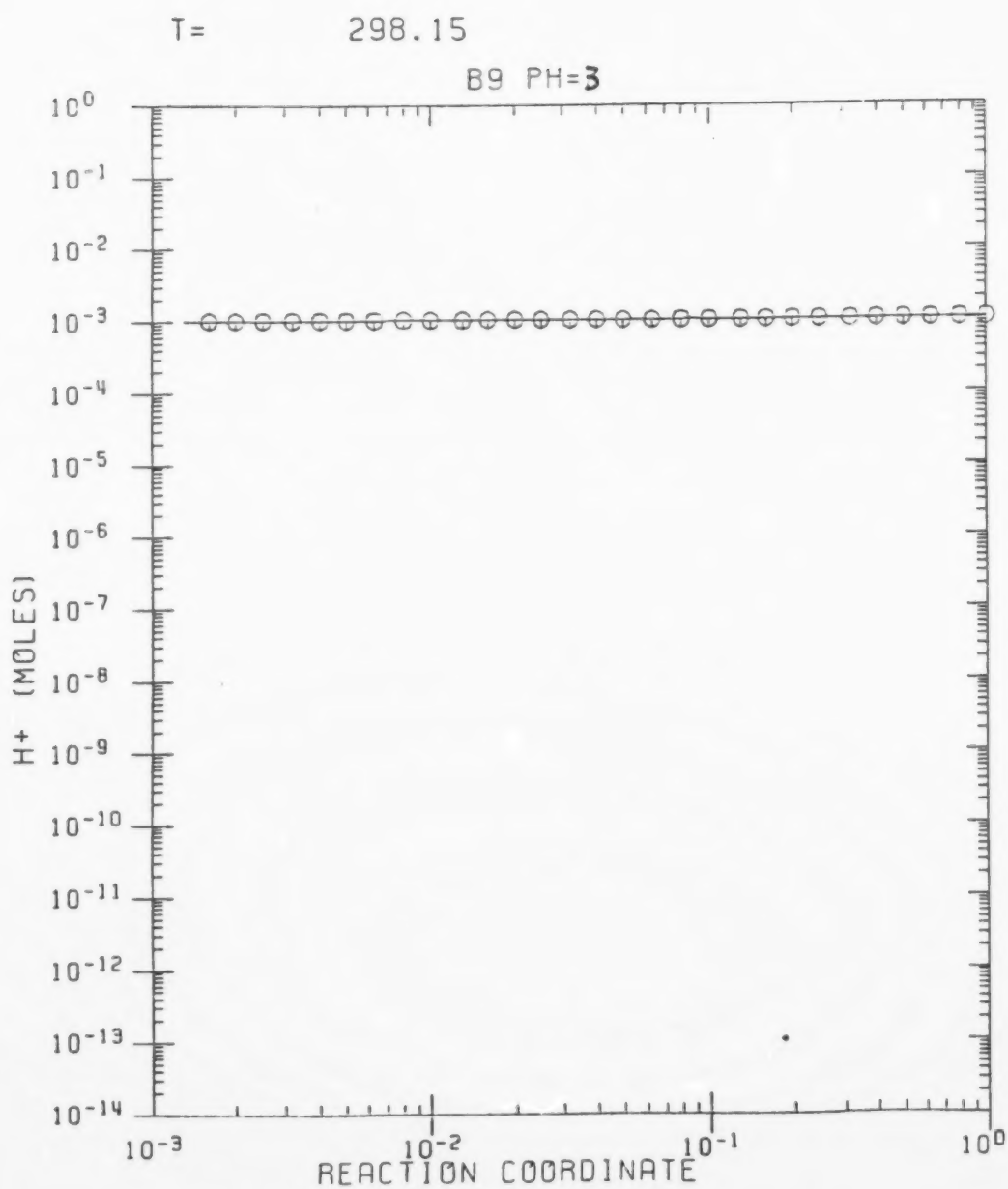


FIGURE 7

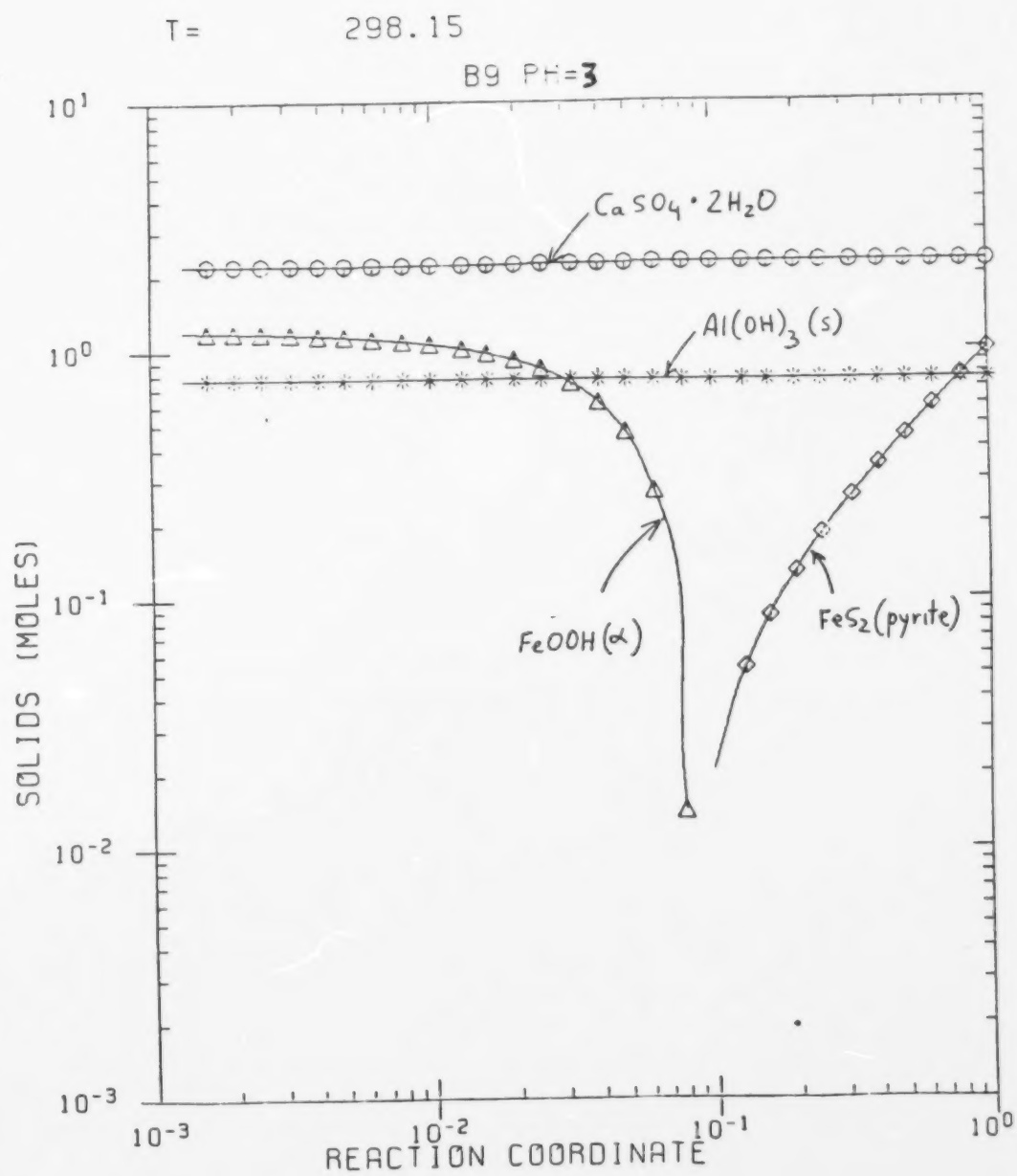


FIGURE 8

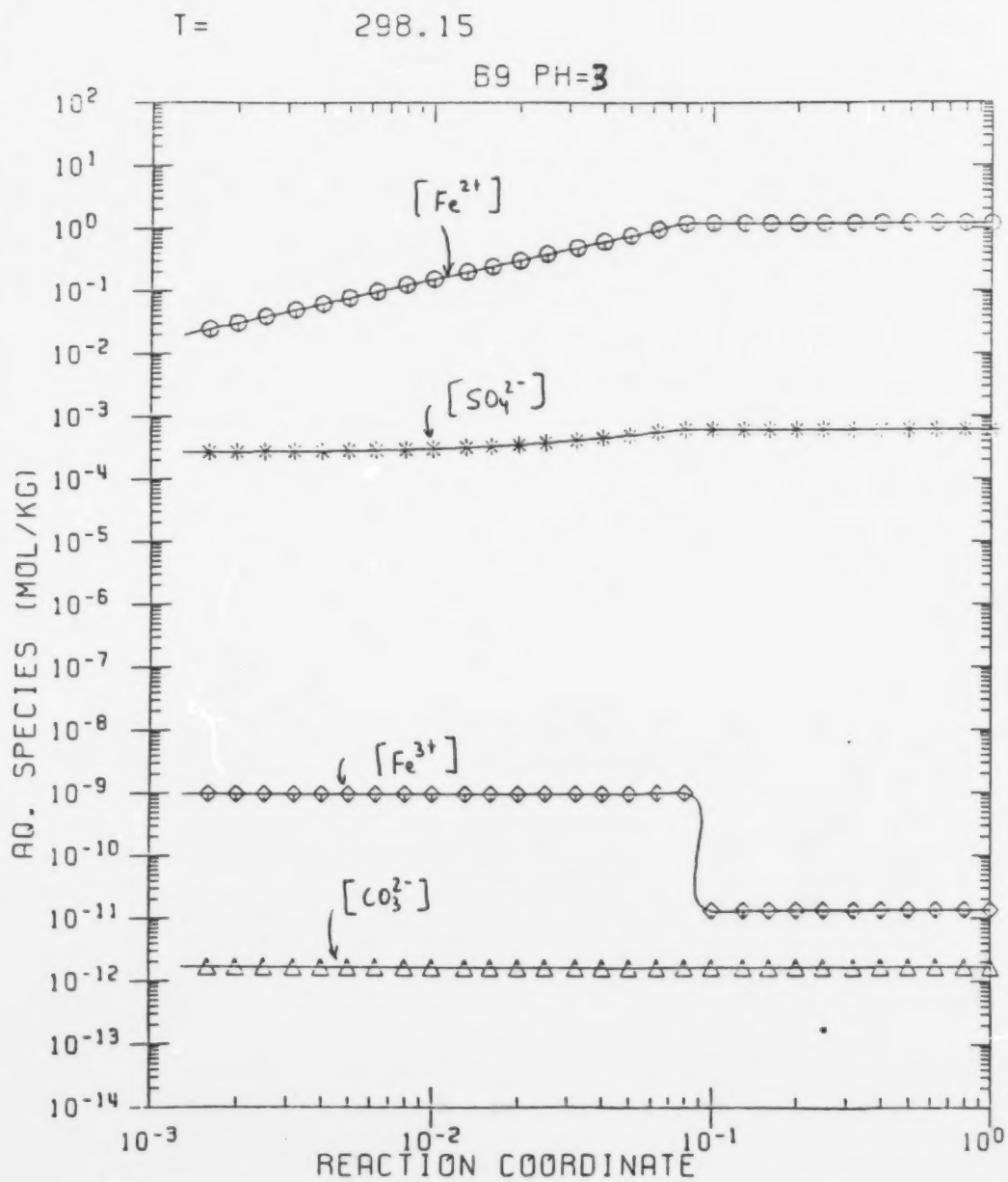
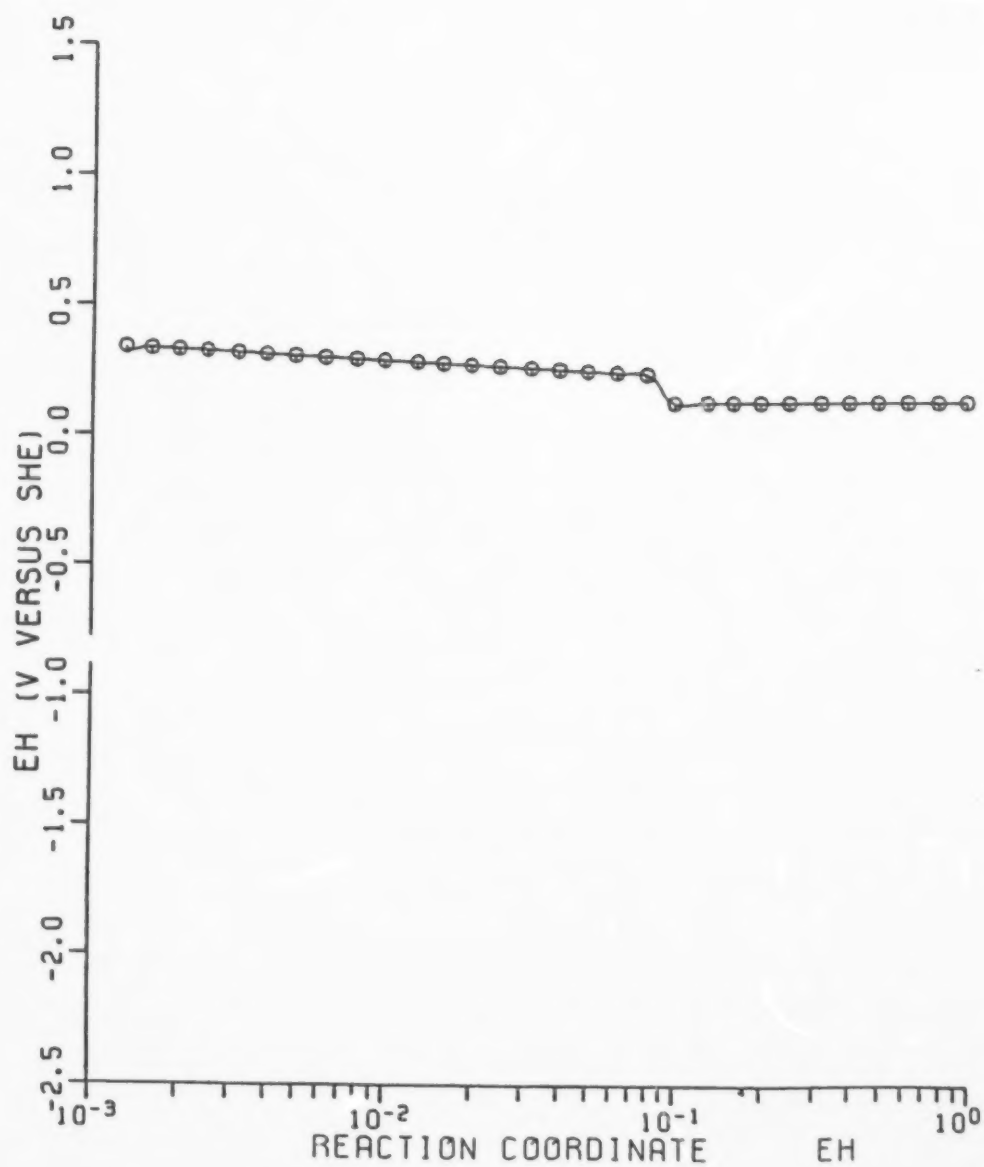


FIGURE 9



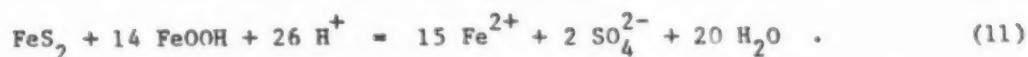
B9 PH=6

FE7S

3.2 TITRATIONS WITH PYRITE AND $O_2(aq)$

3.2.1 Thermodynamic Analysis

In this series of calculations, the titrant is a mixture of pyrite and $O_2(aq)$ with pyrite: $O_2(aq)$ = 14/13:7/2. This ratio was chosen to simulate pH control in the system, by keeping the H^+ concentration close to constant along the reaction path (even in floating pH mode calculations). The ratio of reaction coordinates was derived from the stoichiometry of the following two reactions:



Here we assumed that $O_2(aq)$ reacts preferentially with pyrite. However, the $O_2(aq)$ added to the system via the titrant could a priori participate in either reaction 1 or reaction 2 (see Figure 1).

From a thermodynamic viewpoint,

$$\Delta G_R(1) = \Delta G_R^\circ(1) + 2/7 RT \ln[Fe^{2+}] [SO_4^{2-}]^2 + 4/7 RT \ln[H^+] - RT \ln[O_2(aq)] \quad (12)$$

and

$$\Delta G_R(2) = \Delta G_R^\circ(2) + 4RT \ln[Fe^{3+}] / [Fe^{2+}] - 4RT \ln[H^+] - RT \ln[O_2(aq)] \quad (13)$$

where $\Delta G_R(1)$ is the Gibbs energy change for reaction 1, $\Delta G_R^\circ(1) = -354.33 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta G_R^\circ(2) = -193.12 \text{ kJ}\cdot\text{mol}^{-1}$.

Thus, because $\Delta G_R^\circ(1)$ is much more negative than $\Delta G_R^\circ(2)$, reaction 1 is favoured thermodynamically over reaction 2 under realistic conditions. Therefore, the oxygen added as the titrant participates in reaction 1 (and not in reaction 2). In a kinetic sense, we therefore simulate here a system with $k_1 \gg k_2$.

3.2.2 Floating pH Calculations

In cases B1 and B2, the system initially contains $\text{Fe}(\text{OH})_3$ (amorphous), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), $\text{Al}(\text{OH})_3$ (gibbsite) and CaCO_3 (calcite). The results of the calculation for B1 are shown in Figures 10-12. Case B2 gave similar results. These figures show that the pH does not remain at its initial value ($\text{pH} = 3$), but hovers between 6 and 7 for $\xi < 4 \times 10^{-2}$. This is due to buffering by CaCO_3 . Indeed, in case B13, which is equivalent to case B1 but does not contain gypsum, gibbsite and calcite, the $\text{pH} = 3$ over a large range of the reaction coordinate (see Figures 13 and 14).

It should be noted that, in both cases B1 and B2, the formation of pyrite indicates that the system is not in a partial equilibrium condition and that total equilibrium is achieved early along the reaction path.

3.2.3 Fixed pH Calculations

Case B7 was run at a fixed pH value of 3 (see Figures 15 and 16). It is interesting to compare B7 with the corresponding case (i.e., $\text{pH} = 3$) B9, which was titrated with pyrite and no $\text{O}_2(\text{aq})$. The comparison shows that the addition of $\text{O}_2(\text{aq})$ to the titrant is equivalent to reducing the reaction coordinate by a factor of 1/13 (cf., Figures 7 and 15). This "shift" occurs because the added oxygen is consumed by one mole of pyrite, and therefore only 1/13 mole of pyrite is available for other reactions. The added oxygen cannot be "constrained" or "directed" to react preferentially with Fe^{2+} unless the $\Delta_f G^\circ$ in the database are changed.

In case B7, pyrite does not form because the pH is low and the system is therefore not in full equilibrium. As expected, the abundance of FeOOH decreases along the reaction path due to reaction (11). $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is formed at high sulfate concentrations.

In case B8 ($\text{pH}=6$), the carbonate solids are stable, i.e., FeCO_3 and CaCO_3 exist at equilibrium (see Figure 17) along the reaction path, and the production of Fe^{2+} (via reactions (1) and (11)) results in the

conversion of CaCO_3 to FeCO_3 . In case B8, FeS_2 appears late along the reaction path. Once FeS_2 forms, it is in equilibrium with FeOOH and the increase in Fe^{2+} and SO_4^{2-} due to reaction (1) shifts the equilibrium of reaction (11) to the left and the abundance of FeOOH increases.

FIGURE 10

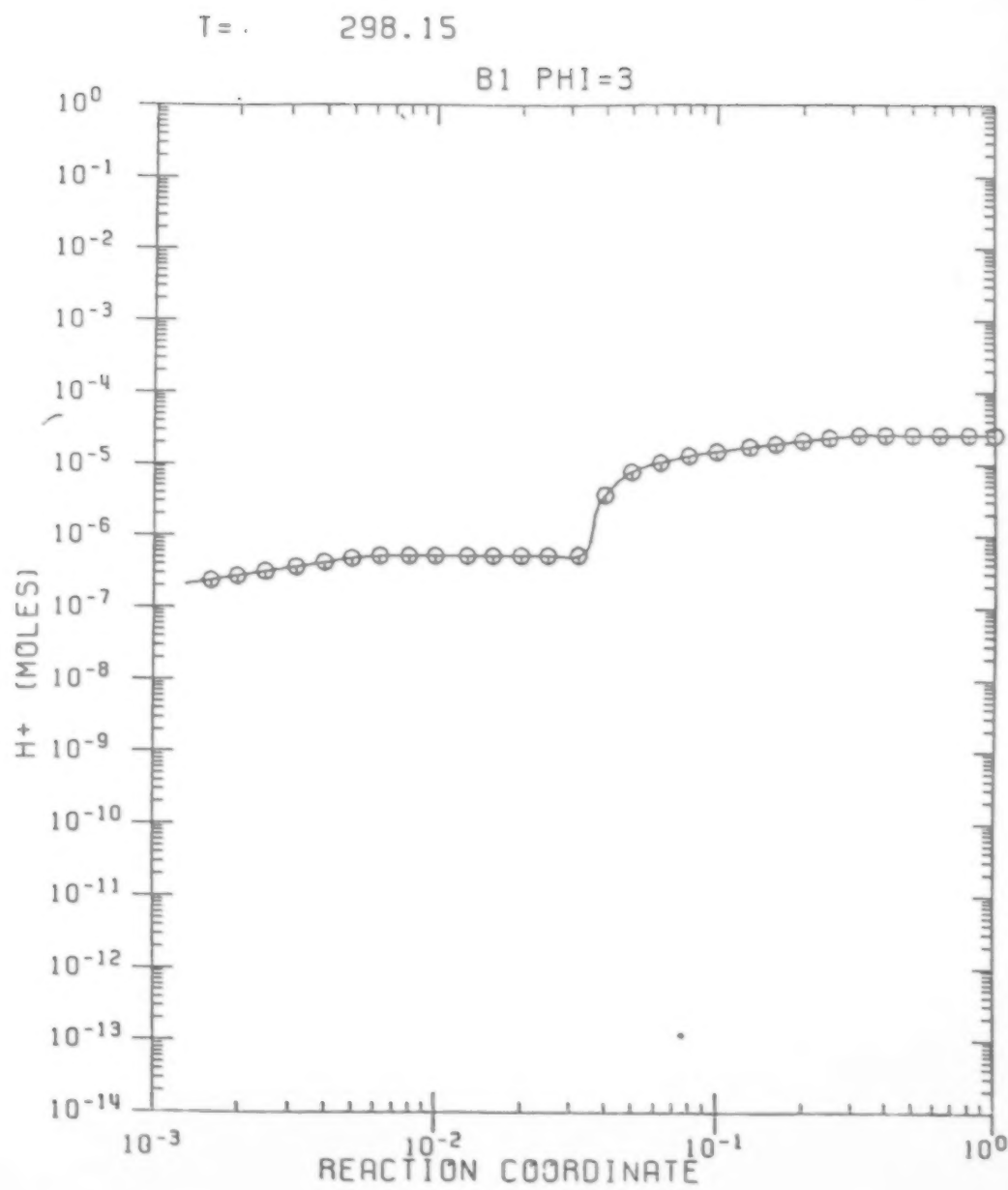


FIGURE II

T = 298.15

B1 PHI=3

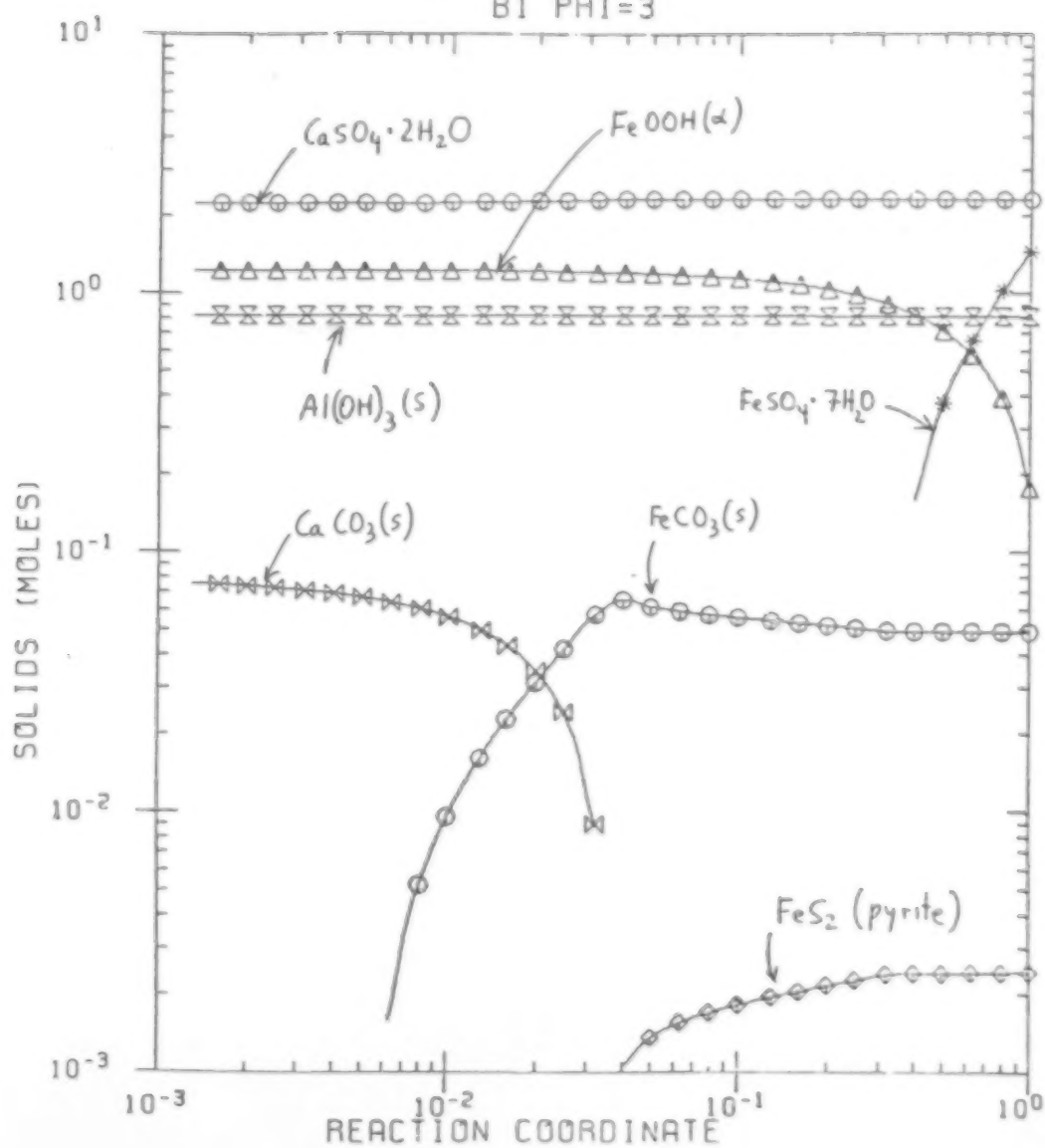


FIGURE 12

T = 298.15

BI PHI=3

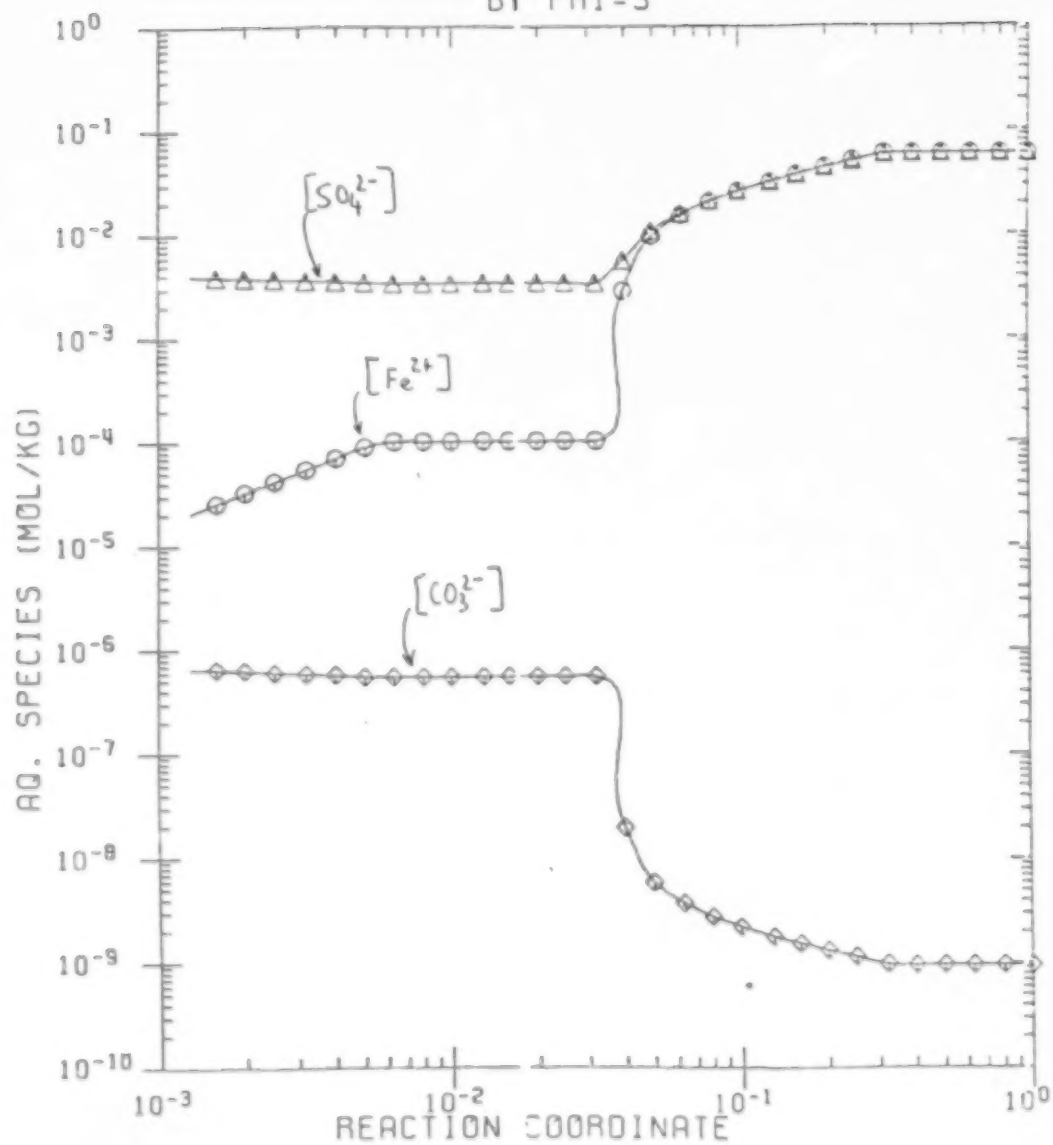


FIGURE 13

T= 298.15

B13 PHI=3

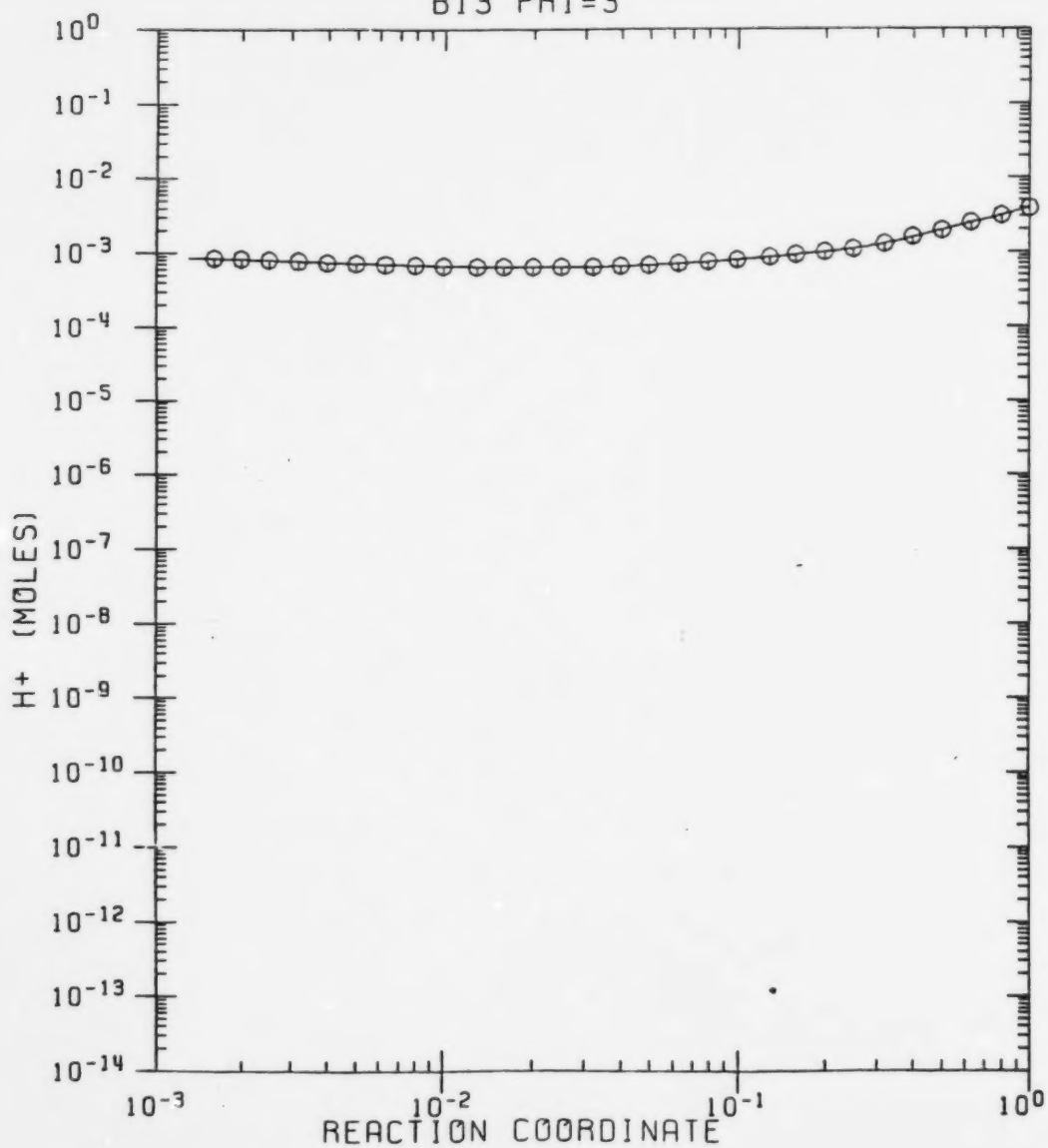


FIGURE 14

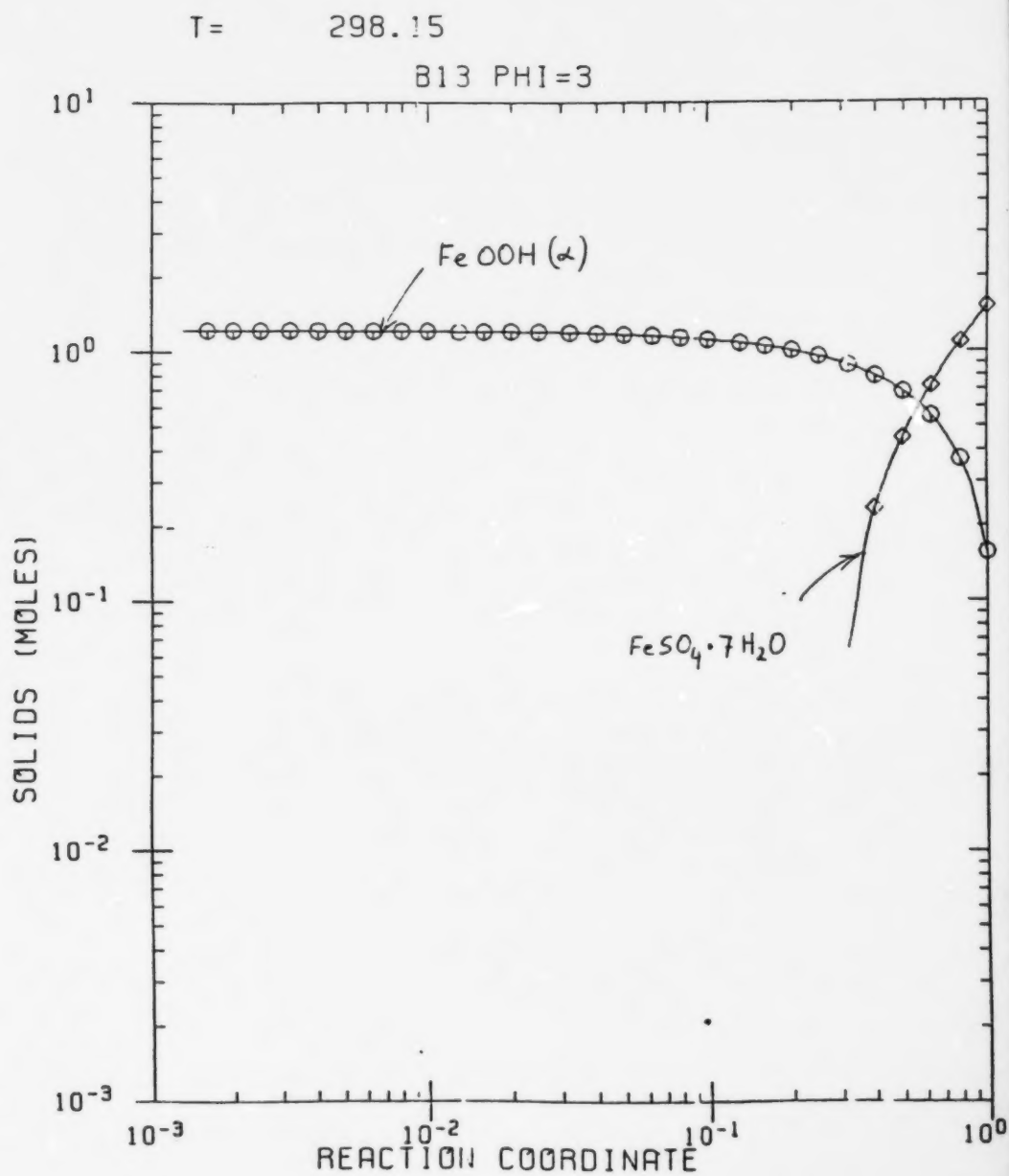


FIGURE 15

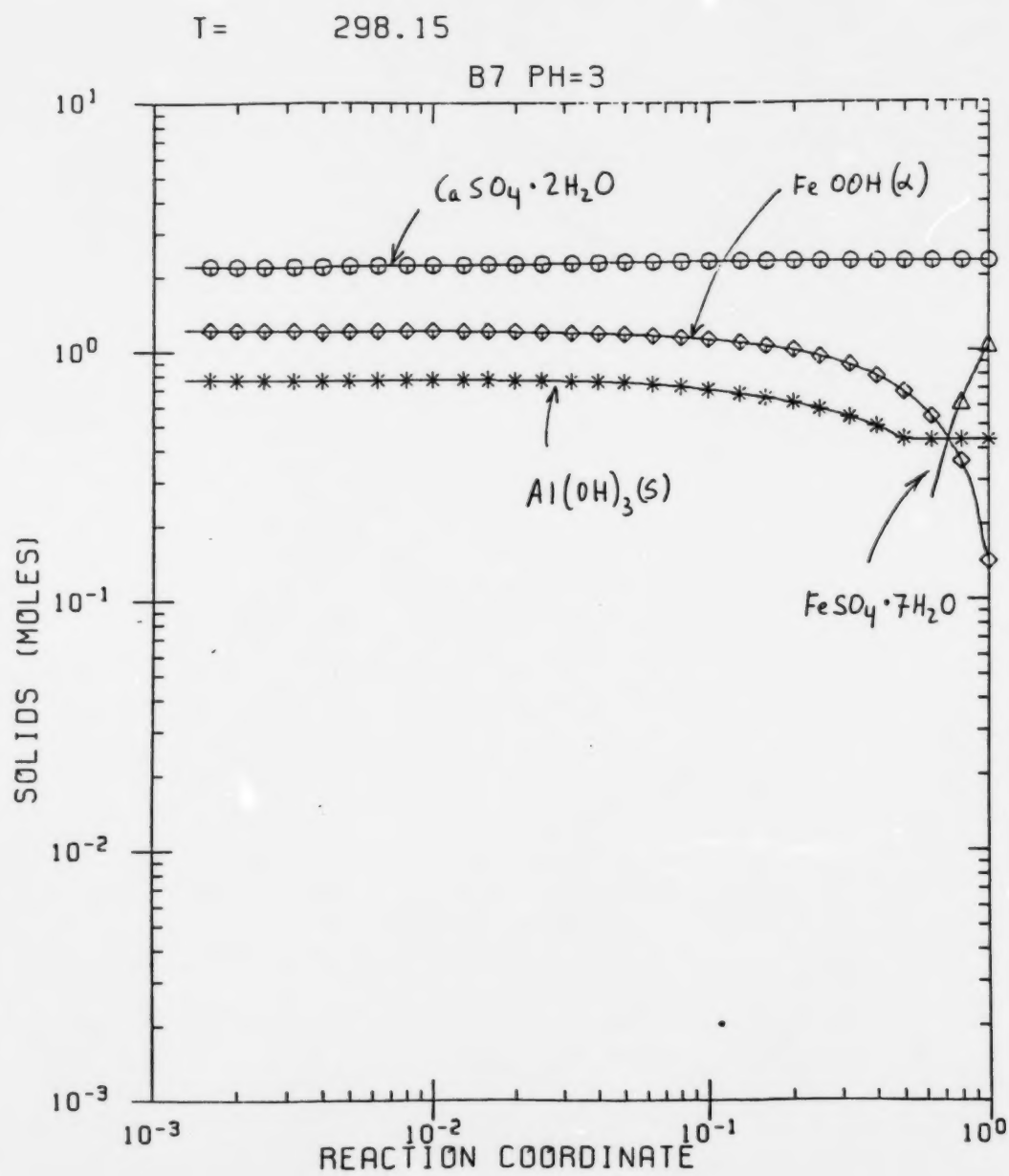


FIGURE 16

T= 298.15

B7 PH=3

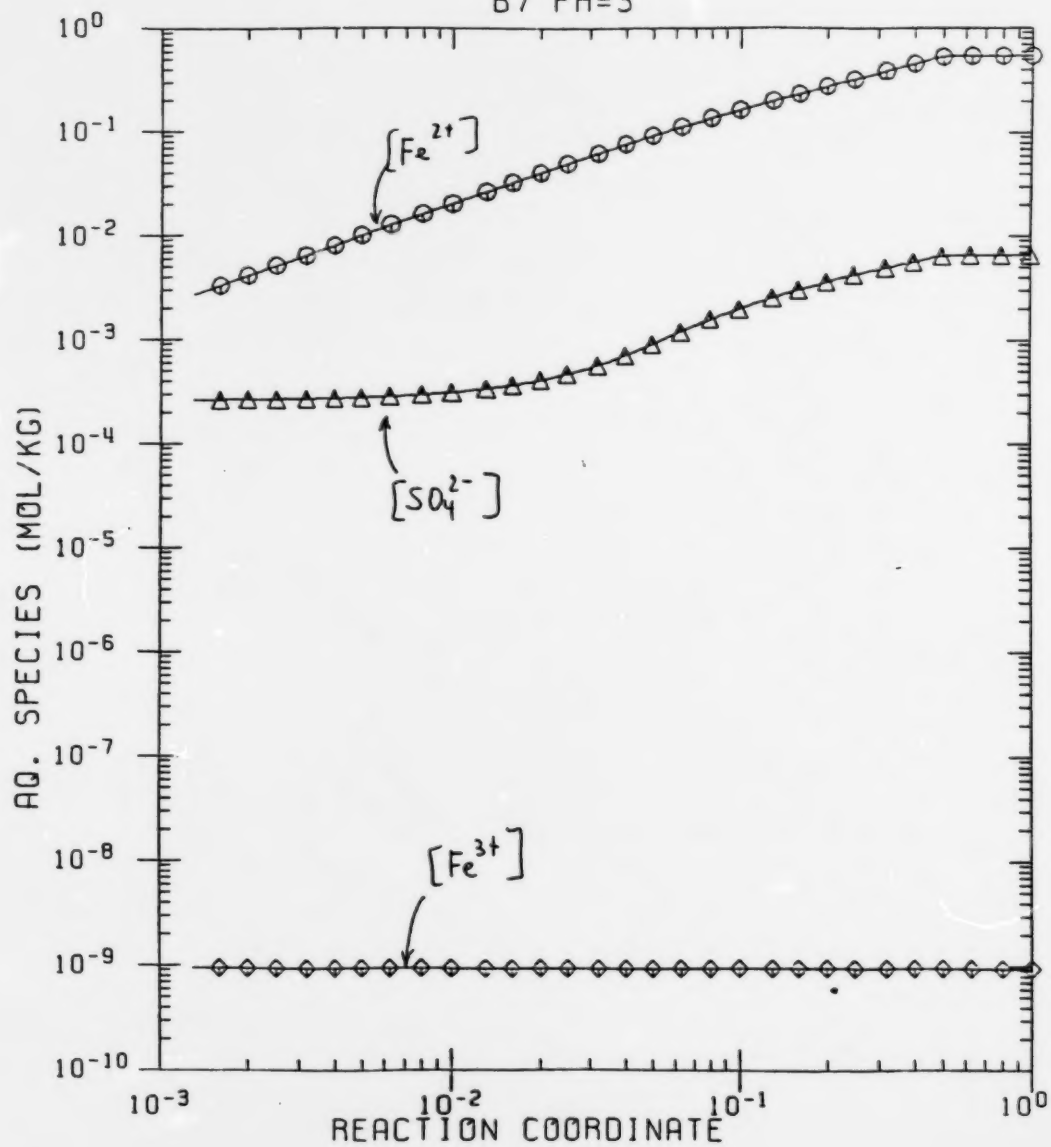
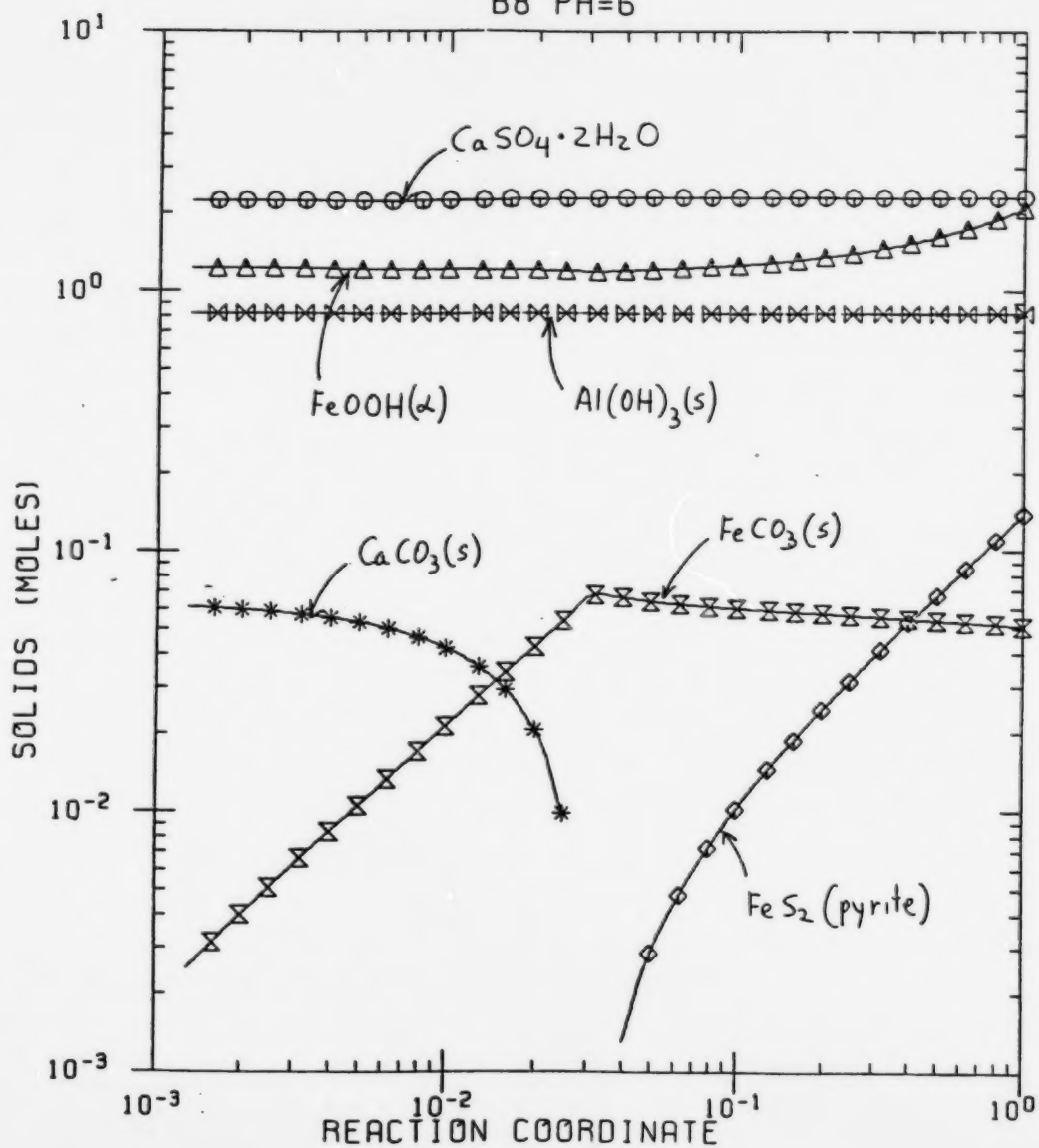


FIGURE 17

T= 298.15

B8 PH=6



3.3 TITRATIONS WITH THE PRODUCTS OF REACTIONS 2 AND 3

In this series of calculations, the titrants are the products of reactions 2 and 3 in the pyrite oxidation cycle (see Figure 1). The relative rates at which the products of the two reactions are added to the system is different in the various calculations described below. These simulations attempt to represent cases with different relative rates k_2 and k_3 .

3.3.1 Simulation of the Case $k_2 = k_3$

In this case, the quantities of the products of reactions 2 and 3 added to the system are calculated by assuming that the net production of Fe^{2+} (from reactions 2 and 3) is zero. A very similar situation was studied in run 4B.1 in Reference 3 and therefore will not be repeated here. The results of this run indicate that (i) the pH is buffered by the solids in the system, (ii) the pH decreases along the reaction path, in essence due to reaction 3, and (iii) FeS_2 does not form (see Figures 18-19).

3.3.2 Simulation in the Case $k_2:k_3 = 1:10$

In case B24 (see Figure 20), we want reaction 3 to produce Fe^{2+} 10 times faster than it is consumed by reaction 2. We also assume that Fe^{3+} and $\text{Fe}(\text{OH})_3(\text{am})$ are in rapid equilibrium. This simulation requires the following titrant composition: $1.35 \text{ Fe}^{2+} - 1.25 \text{ Fe}(\text{OH})_3 + 2.3 \text{ OH}^- + 0.2 \text{ SO}_4^{2-}$. Case B24 was run in a floating pH mode with $\text{pH}_1 = 7$. The system rapidly reaches equilibrium with pyrite (see Figure 21).

We attempted to impose disequilibrium by deleting FeS_2 , FeS and Fe_7S_8 from the database. However, this resulted in precipitation of Fe_3O_4 (case B27). The pH changes from approximately 7 to approximately 6 along the reaction path in B24. We checked whether the formation of pyrite (case B24) and of Fe_3O_4 (case B27) was due to the relatively high pH conditions by running a similar case in a fixed pH mode, at $\text{pH} = 3$ (case B29). The results are shown in Figure 22. Indeed, in this case no iron oxides are formed and there is no equilibrium with pyrite. As expected, FeOOH gradually dissolves due to the reaction with pyrite.

FIGURE 18

T= 298.15 K

BEAK CASE 4B.1

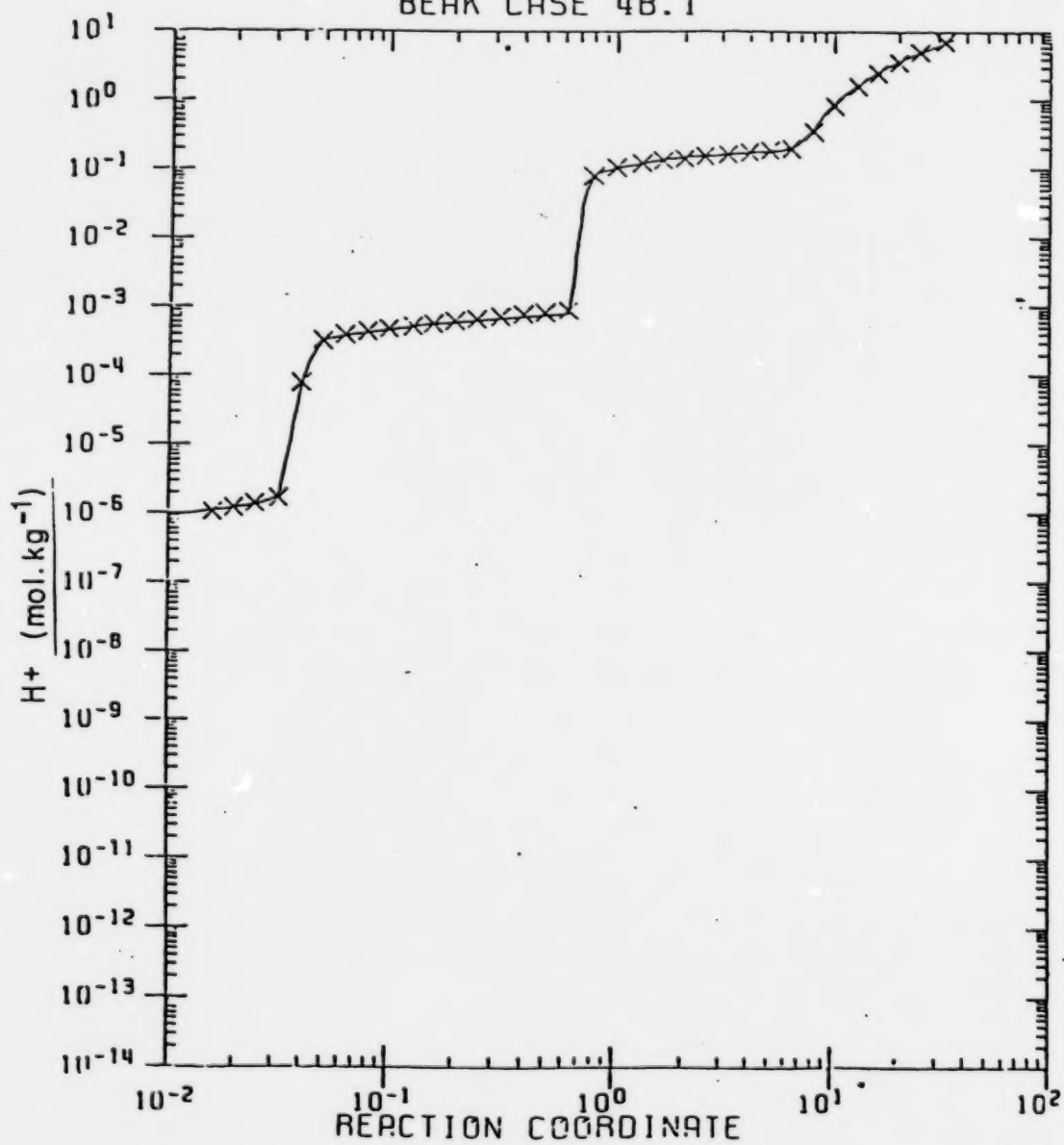
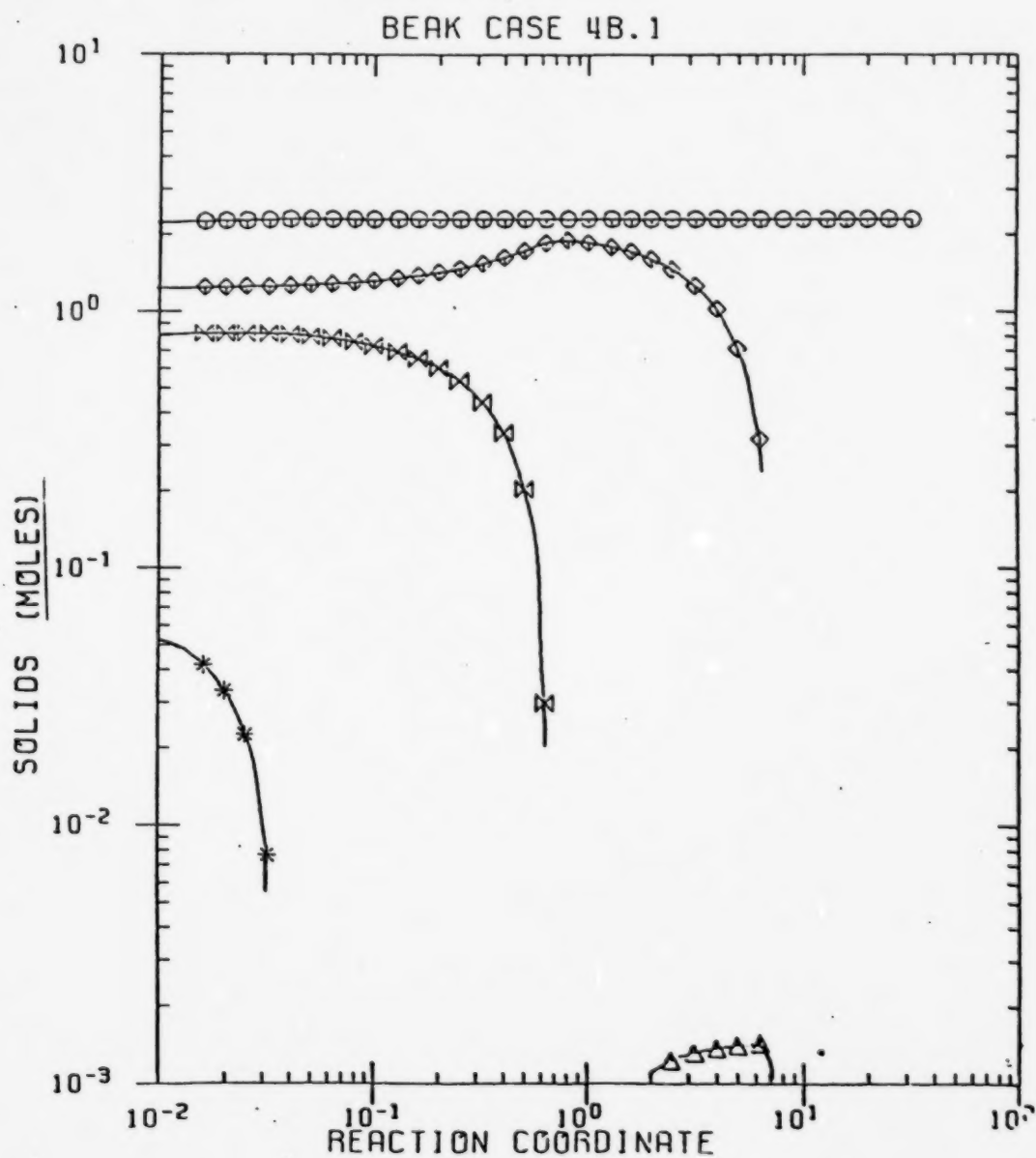


Figure 19: The abundances of solids as a function of the reaction coordinate, for case 4B.1.

$\circ$ - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\diamond$ - $\text{FeOOH}(\alpha)$, $*$ - CaCO_3 (s)
 Δ - jarosite, ∇ - $\text{Al}(\text{OH})_3$ (gibbsite)

T = 298.15 K



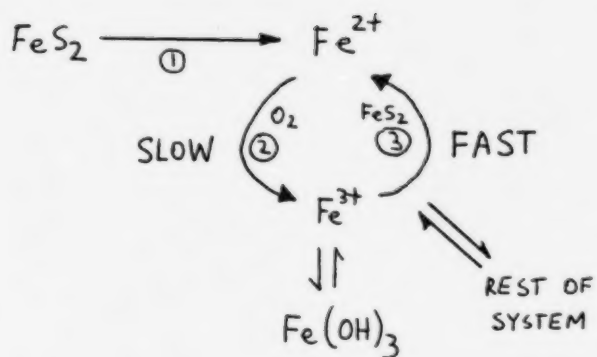


Figure 20. The Case $k_2:k_3 = 1:10$

FIGURE 21

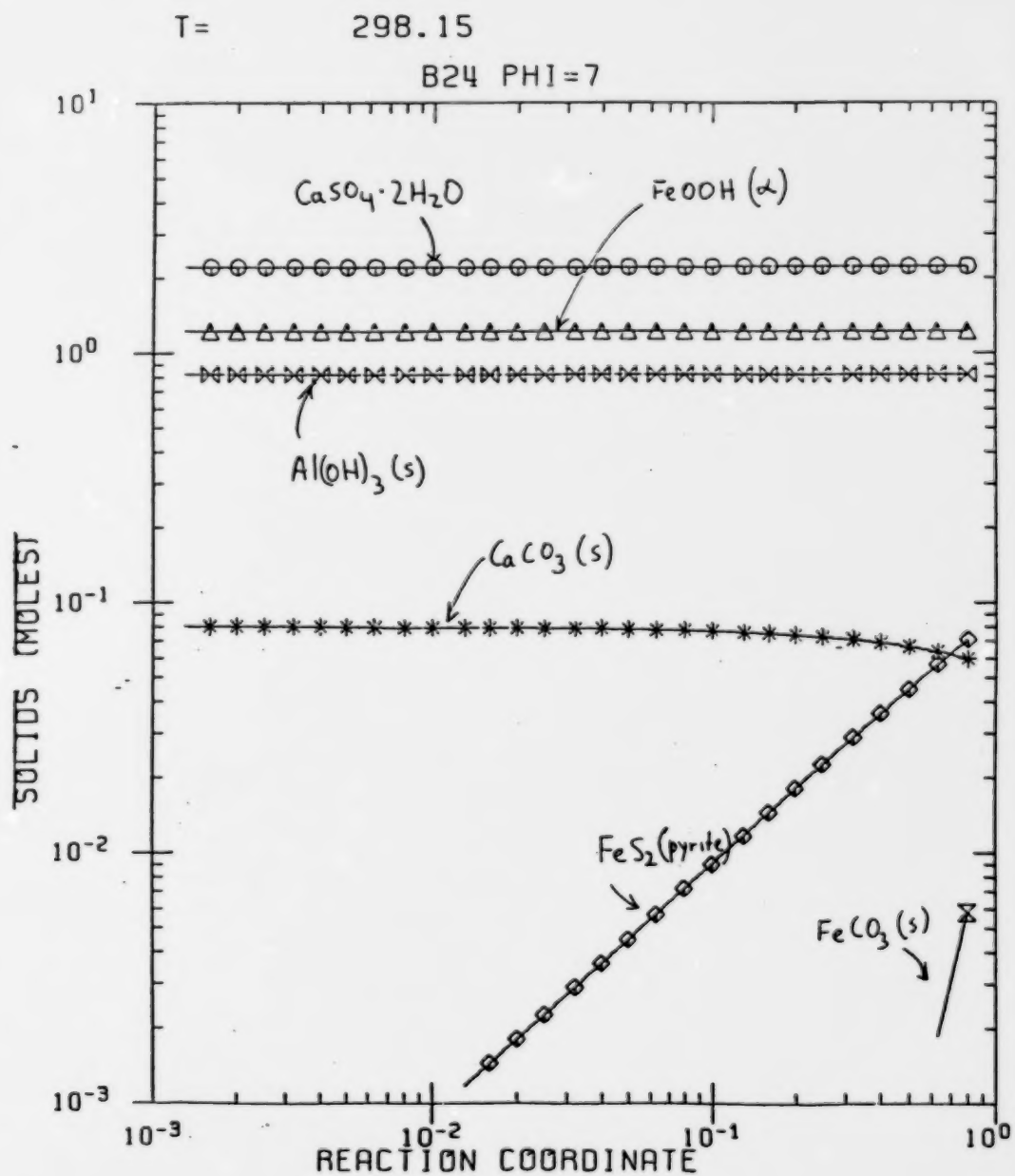
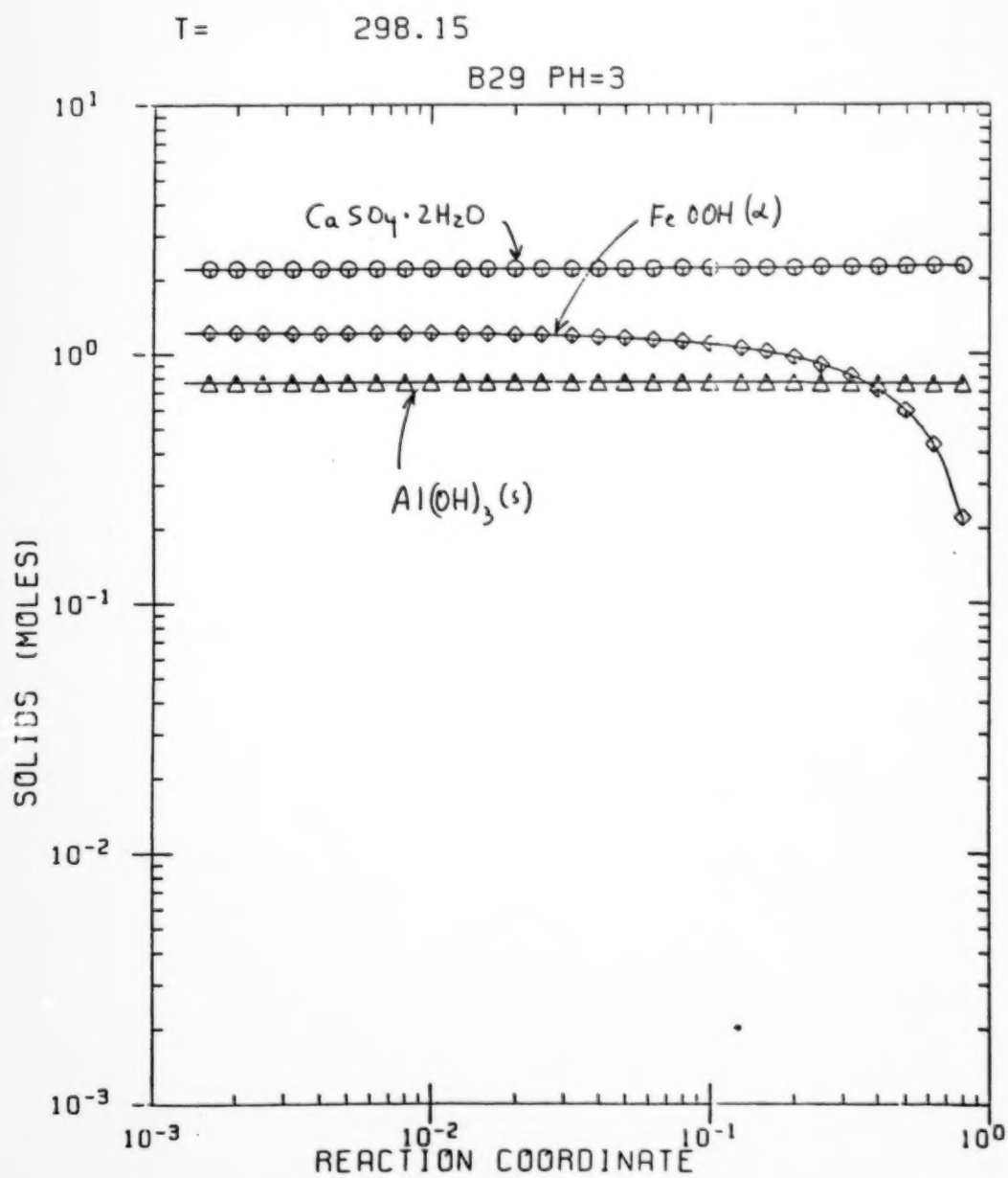


FIGURE 22



3.4 TITRATION WITH H^+

A titration with H^+ was carried out (case B23) to study the buffering effect of the solids in the system. This is required in order to carry out the kinetic calculations described in Section 2 as a function of pH. The results are shown in Figures 23-25. These calculations show that $CaCO_3$ (calcite) buffers the system at $pH \approx 6$, $Al(OH)_3$ (gibbsite) buffers the system at $pH \approx 3$ and $FeOOH$ (goethite) buffers the system at $pH \approx 0$. Also, as expected, the SO_4^{2-} and CO_3^{2-} concentrations decrease as the pH becomes more acidic.

FIGURE 23

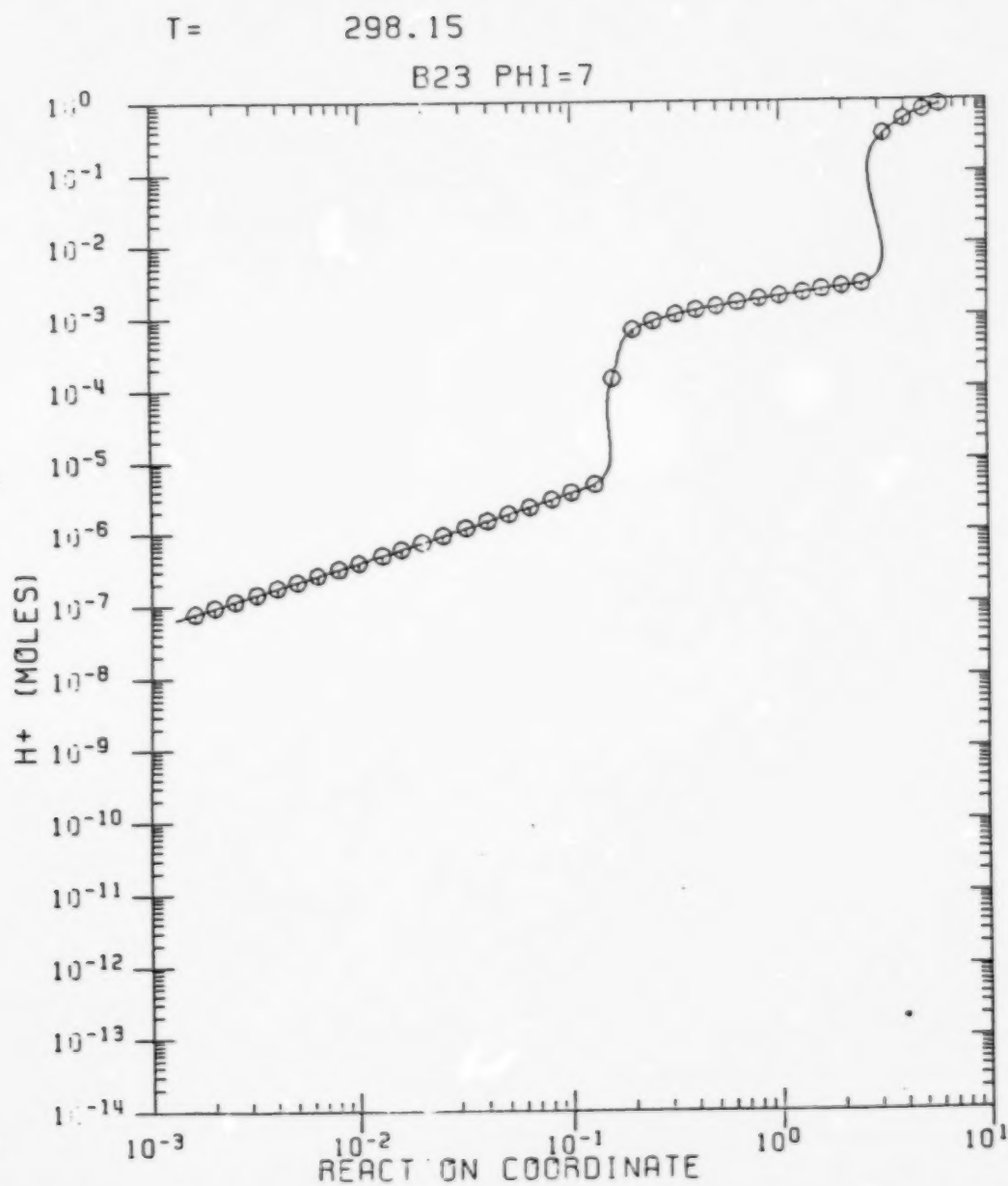


FIGURE 24

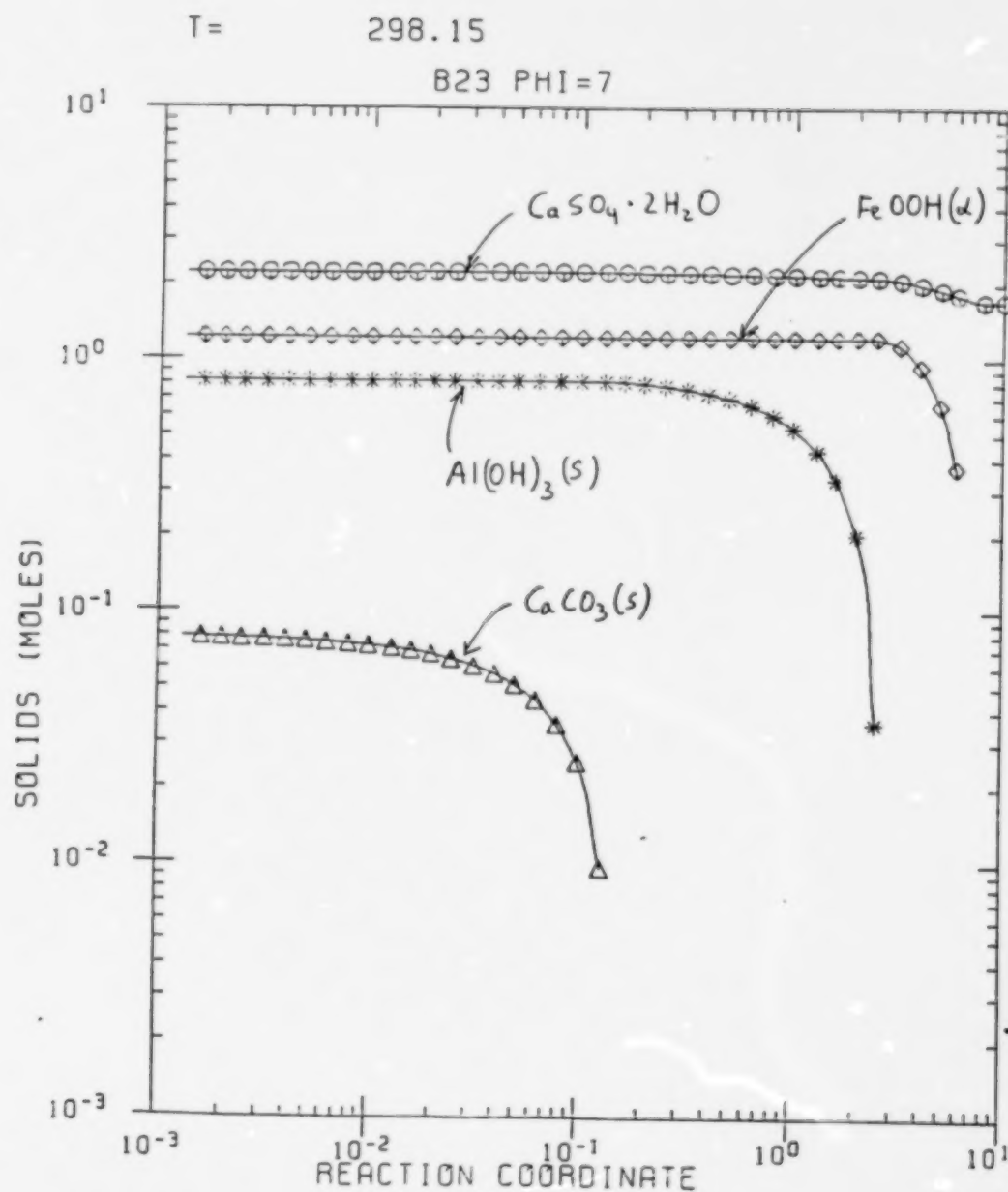
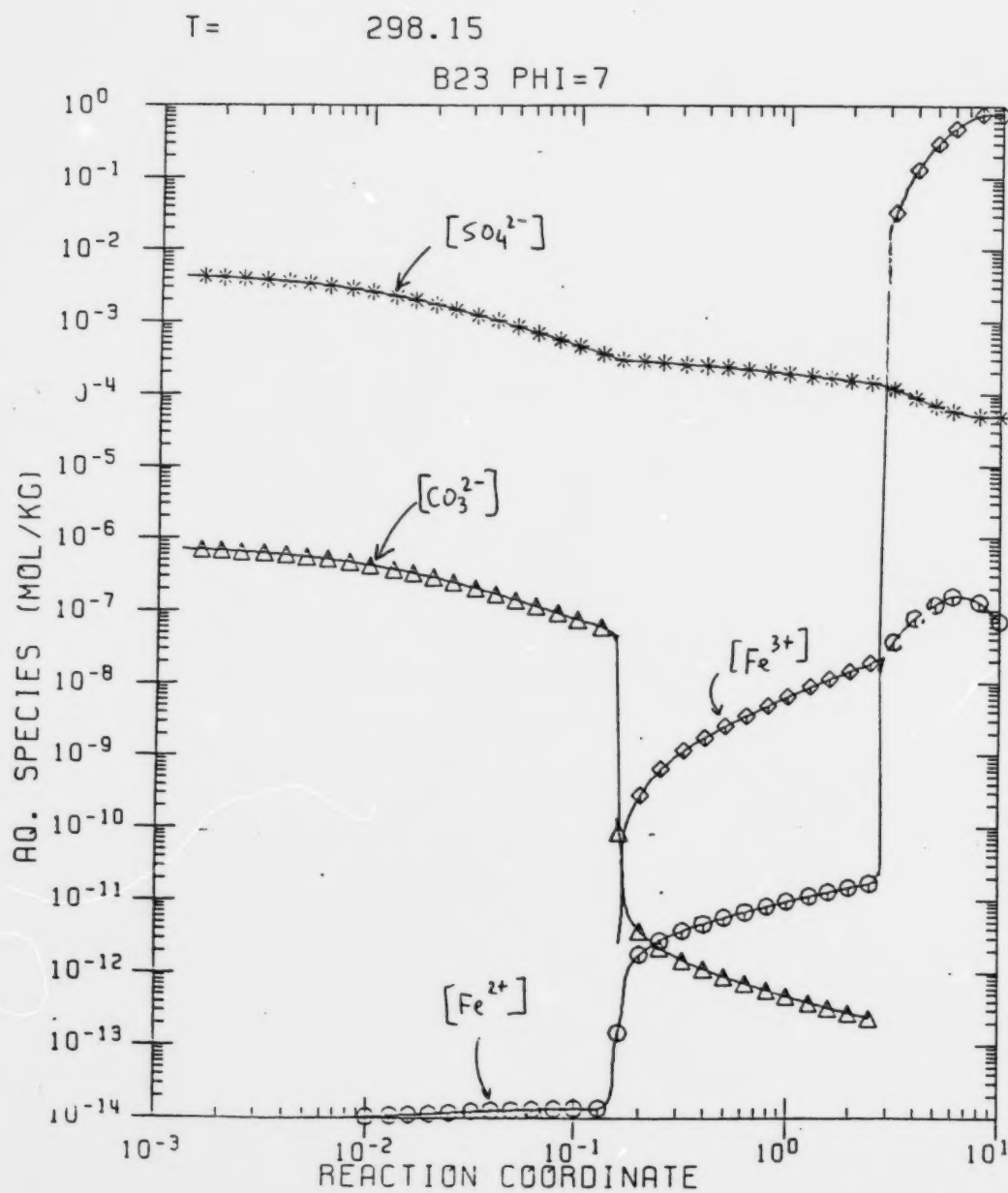


FIGURE 25



4. CONCLUSIONS

The calculations in this report simulate the oxidative dissolution of pyrite under partial-equilibrium conditions. A simple kinetic model for the system was presented in Section 2. More sophisticated kinetic models for this system are unwarranted at present since kinetic data are scarce [7]. In particular, it is not practical, at present, to attempt to couple the pyrite system ($\text{Fe-S-O}_2\text{-H}_2\text{O}$) to the rest of the mineral assemblage in the tailings via a kinetic scheme. We have therefore also performed reaction path calculations (see Section 3), which take into account the coupling of the pyrite system to the other minerals in the tailings. The kinetic approach and the reaction path approach should be used in tandem to simulate the behaviour of pyritic tailings.

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APPENDIX.

THE THERMODYNAMIC DATABASE

SPECIES	$\Delta_f G^\circ$ (kJ·mol ⁻¹)
H+	0.0
H2O	-237.18
OH-	-157.34
Ca+2	-552.8
Fe+2	-91.21
Fe+3	-16.82
CO3-2	-527.99
HCO3-	-586.95
H2CO3	-623.20
SO4-2	-744.54
HSO4-	-755.88
S-2	85.81
HS-	12.18
H2S(AQ)	-27.91
S2-2	82.63
FeOH+	-274.1
Fe(OH)2(AQ2)	-447.9
Fe(OH)3-	-625.6
Fe(OH)4-2	-777.2
FeOH+2	-241.4
Fe(OH)2+	-458.7
Fe(OH)3(AQ)	-660.
Fe(OH)4-	-842.
Fe2(OH)2+4	-491.1
Fe3(OH)4+5	-963.0
Fe(OH)2(S)	-492.9
FeOOH(ALFA)	-491.3
Fe(OH)3AMF	-701.18
Fe2O3ALFA	-744.12
Fe3O4(S)	-1018.17
FeCO3(S)	-677.65
FeSO4(S)	-820.6
FeSO4.7H2O	-2510.0
Fe2SO43(S)	-2251.
FeSO4(AQ)	-848.3
FeSO4+	-785.0
Fe(SO4)2-	-1536.6
FeS2(PYRIT)	-160.06
FeS	-102.14
Fe7S8(S)	-854.9

THE THERMODYNAMIC DATABASE (cont.)

SPECIES	$\Delta_f G^\circ$ (kJ·mol ⁻¹)
CAO	-603.48
CAOH+	-717.6
CA(OH)2(S)	-898.68
CAC03(AQ)	-1098.8
CAHC03+	-1146.2
CAC03(S)	-1128.9
CAS04(AQ)	-1310.5
CAS04(S)	-1322.5
CAS042H2O	-1798.2
CAS	-473.
CAFE204	-1414.6
O2(AQ)	16.32
K+	-282.47
K-JAROSITE	-3297.
AL(OH)3GIB	-1154.9
AL+3	-486.4
ALOH+2	-695.1
AL(OH)2+	-902.9
AL(OH)4-	-1308.6
ALS04+	-1248.1
AL(S04)2-	-2003.4